valence from 4+ to 3+. The advantages of NTP as an AIB negative active material include a relatively high specific capacity, its chemical and thermal stability, fabrication from inexpensive precursors, suitably negative redox potential, and high theoretical specific capacity of 133mAh/g. Disadvantages include an inherent lack of electronic conductivity and redox potential that, in the case of aqueous electrolytes, is low enough that some hydrogen evolution from water splitting is likely. The first disadvantage requires producing NTP as with some form of intimate carbon (e.g., carbon black, graphite, carbon nanotubes) to overcome the low electronic conductivity, which necessarily reduces the actual specific capacity. This requirement adds complexity to the manufacturing of NTP at an industrial scale to balance energy density with electrical conductivity on the bulk, micro, and nano-scales.

SUMMARY

[0008] A general example of the present disclosure involves the industrial manufacture of NTP using a variety of precursors and processes that consolidate the precursor materials, thermally treat said precursors into crystalline, functional NTP material, and impart electronic conductivity through the intimate association of the NTP with some form of conductive carbon. Various options exist for accomplishing these steps, including the consolidation of one or more steps into a single step to simply the manufacturing process. However, all of the various combinations of precursors, manufacturing methods, and individual process steps have trade-offs that affect one or more of the following: control over NTP quality, active material costs, capital equipment expense, and operating expense for the processes. A careful understanding of these will facilitate the effective scale-up of NTP fabrication to support projected volumes of AIB sales into the GWh/yr scale.

[0009a] In one aspect, the present disclosure provides a method of preparing carbon-coated ~~synthesizing~~ sodium titanium phosphate hollow spheres for use in an electrochemical device, said method comprising process A or process B, wherein process A comprises steps ~~comprising:~~ (a) mixing a carbon source, a surfactant and ~~homogenizing two or more~~ pre-cursors of titanium, sodium and phosphate in proportions ~~related~~ according to the desired reaction stoichiometry to form a wet aqueous ~~or dry~~ mixture, (b) homogenizing said aqueous mixture ~~consolidating the precursor mixture~~ by spray drying in air to form hollow spheres, and ~~if a wet~~

homogenization was used, (c) annealing said hollow spheres at 700-900°C to give carbon-coated sodium titanium phosphate hollow spheres, and process B comprises steps (i) mixing a carbon source, a surfactant and part of the precursors of titanium, sodium and phosphate as a wet aqueous mixture; (ii) homogenizing said aqueous mixture by spray drying in air to form hollow spheres which are then consolidated with any remaining precursors of titanium, sodium and phosphate to form a mixture, and (iii) annealing said mixture at 700-900°C to give carbon-coated sodium titanium phosphate hollow spheresthermally treating the obtained precursor mixture, wherein conductive carbon and/or conductive carbon pre-cursor is introduced in at least one of the steps a)-c).

[0009b] In another aspect, the present disclosure provides carboncoated sodium titanium phosphate hollow spheres prepared by the method an electrochemical device produced by the method as disclosed herein.

[0009c] In another aspect, the present disclosure provides an electrochemical device comprising electrodes made from the carbon-coated sodium titanium phosphate hollow spheres as disclosed herein.

[0009] Several key descriptions of NTP fabrication are provided in the patent an academic literature which warrant review:

[0010] Although the first NTP synthesis can be traced back to the late 1800's, the first discussion of its ability to intercalate Na+ was provided by Delmas et al.[1] In this work, NTP was synthesized via the reaction:

$$Na_2CO_3 + 4TiO_2 + 6(NH_4)_2HPO_4 \rightarrow 2NaTi_2(PO_4)_3 + 9H_2O + CO_2 + 12NH_3$$

[1] Mat. Res. Bull., Vol. 22, 631-639 (1987)

CLAIMS

I/We claim:

1. A method of preparing carbon-coated ~~synthesizing~~ sodium titanium phosphate hollow spheres for use in an electrochemical device, said method comprising process A or process B,

wherein process A comprises steps ~~comprising:~~ (a) ~~homogenizing two or more~~ mixing a carbon source, a surfactant and pre-cursors of titanium, sodium and phosphate in proportions ~~related~~ according to the desired reaction stoichiometry to form a wet aqueous~~or dry~~ mixture, (b) homogenizing said aqueous mixture ~~consolidating the precursor mixture~~ by spray drying in air to form hollow spheres, and~~if a wet homogenization was used,~~ (c) annealing said hollow spheres at 700-900°C to give carbon-coated sodium titanium phosphate hollow spheres,~~thermally treating the obtained precursor mixture, wherein conductive carbon and/or conductive carbon pre-cursor is introduced in at least one of the steps a)-c)~~

and process B comprises steps (i) mixing a carbon source, a surfactant and part of the precursors of titanium, sodium and phosphate as a wet aqueous mixture; (ii) homogenizing said aqueous mixture by spray drying in air to form hollow spheres which are then consolidated with any remaining precursors of titanium, sodium and phosphate to form a mixture, and (iii) annealing said mixture at 700-900°C to give carbon-coated sodium titanium phosphate hollow spheres.

~~2. The method of claim 1, wherein step c) comprises thermally treating the obtained precursor mixture at a shorter time and lower temperature to remove gaseous decomposition by-products, and then at a higher temperature and longer time to effect reaction to crystalline NTP.~~

~~3~~2. The method of claim 1, wherein the precursors comprise titanium dioxide, ammonium di-hydrogen phosphate, and sodium carbonate in a proportion represented by the chemical equation 4 TiO_2 + 6 (NH_4) H_2PO_4 + Na_2CO_3 → 2 $NaTi_2(PO_4)_3$ + 6 NH_3 + 9 H_2O + CO_2.

~~4~~3. The method of claim 1, wherein the precursors comprise titanium dioxide, di-ammonium hydrogen phosphate, and sodium carbonate in a proportion represented by the chemical equation 4 TiO_2 + 6 $(NH_4)_2HPO_4$ + Na_2CO_3 → 2 $NaTi_2(PO_4)_3$ + 12 NH_3 + 9 H_2O + CO_2.

~~5~~4. The method of claim 1, wherein the precursors comprise titanium dioxide, ammonium di-hydrogen phosphate, and sodium di-hydrogen phosphate in a proportion represented by the chemical equation 2 TiO_2 + 2 $(NH_4)H_2PO_4$ + NaH_2PO_4 → $NaTi_2(PO_4)_3$ + 2 NH_3 + 4 H_2O.

~~6~~5. The method of claim 1, wherein the precursors comprise titanium dioxide, sodium phosphate, and phosphoric acid in a proportion represented by the chemical equation 2 TiO_2 + 1/3 Na_3PO_4 + 8/3 H_3PO_4 → $NaTi_2(PO_4)_3$ + 4 H_2O.

~~7~~6. The method of claim 1, wherein the precursors comprise titanium phosphate, sodium di-hydrogen phosphate, and sodium carbonate in a proportion represented by the chemical equation 2 $Ti_3(PO_4)4$ + NaH_2PO_4 + Na_2CO_3 → 3 $NaTi_2(PO_4)_3$ + H_2O + CO_2.

7. The method of claim 1, wherein precursors of titanium are selected from TiO_2, $Ti(OH)_4$ and $Ti_3(PO_4)_4$.

~~8. The method of claim 1, wherein step a) comprises hydrolyzing a titanium-bearing pre-cursor to form a partially hydrolyzed titanium species TiOxHy, sodium hydroxide, and phosphoric acid.~~

~~9. The method of claim 1, wherein step a) comprises homogenizing the pre-cursors into water as a main mixing & solubilizing medium, wherein at least one of a water-soluble and water-insoluble carbon-containing species is also added.~~

~~10~~8. The method of claim ~~9~~1, wherein said ~~the insoluble form of~~ carbon source is selected from ~~includes~~ high surface area carbon, graphite, graphene, ~~or~~ and carbon nanotubes.

~~11~~9. The method of claim ~~10~~1, wherein said ~~the soluble~~ carbon source is introduced as a ~~included in the~~ water mixture ~~in the form~~ of glucose, sucrose, or fructose.

~~12. An electrochemical device produced by any one of the methods of claims 1-11.~~

10. Carbon-coated sodium titanium phosphate hollow spheres prepared by the method of any one of claims 1-9.

11. An electrochemical device comprising electrodes made from the carbon-coated sodium titanium phosphate hollow spheres of claim 10.