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 sodium titanium phosphate hollow spheres for use in an electrochemical device, said method comprising process A or process B, wherein process A comprises steps (a) mixing a carbon source, a surfactant and pre-cursors of titanium, sodium and phosphate in proportions according to the desired reaction stoichiometry to form a wet aqueous mixture, (b) homogenizing said aqueous mixture by spray drying in air to form hollow spheres, and

(c) annealing said hollow spheres at 700-900^{o}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^{o}C to give carbon-coated sodium titanium phosphate hollow spheres.

[0009b] In another aspect, the present disclosure provides carboncoated sodium titanium phosphate hollow spheres prepared 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 sodium titanium phosphate hollow spheres for use in an electrochemical device, said method comprising process A or process B,

wherein process A comprises steps (a) mixing a carbon source, a surfactant and pre-cursors of titanium, sodium and phosphate in proportions according to the desired reaction stoichiometry to form a wet aqueous mixture, (b) homogenizing said aqueous mixture by spray drying in air to form hollow spheres, and (c) annealing said hollow spheres at 700-900^{o}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^{o}C to give carbon-coated sodium titanium phosphate hollow spheres.

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 $4\ TiO_2 + 6\ (NH_4)\ H_2PO_4 + Na_2CO_3 \rightarrow 2\ NaTi_2(PO_4)_3 + 6\ NH_3 + 9\ H_2O + CO_2$.

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

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.

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.

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 said carbon source is selected from high surface area carbon, graphite, graphene, and carbon nanotubes.

9. The method of claim 1, wherein said carbon source is introduced as a water mixture of glucose, sucrose, or fructose.

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.