

METHODS FOR NTP MANUFACTURING

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority to U.S. Provisional Patent Application No. 62/831,077, filed on April 8, 2019, which is hereby incorporated by reference in its entirety.

TECHNICAL FIELD

[0002] The current invention applies to the field of secondary batteries, specifically those employing aqueous electrolytes and ceramic intercalation materials. This combination is referred to as aqueous intercalation battery (AIB) materials and devices.

BACKGROUND

[0003] Economic, widespread implementation of renewable energy using sustainable technologies, such as solar or wind, require the safe, efficient, cost-effective, and durable storage of electrical energy. The requirements for battery technologies in these applications are very stiff. Batteries must be provided at installed costs of ~\$100/kWh and must be capable of 20yr lifetime with daily cycling to >85% DOD. Also, they must exhibit a general insensitivity to the ambient conditions, such as no loss of cycle life in hot climate applications. Although several battery technologies are available to perform these functions, those made at adequate manufacturing scale suffer from some key drawbacks.

[0004] By far the most widespread technology installed for these applications is lithium ion battery (LIB) technology. This class of batteries actually encompasses a broad set of options for anode and cathode materials to achieve different metrics, but generally there exists tradeoffs between cost, safety, energy density, and cycle life. LIB technologies that can leverage economies-of-scale for electric vehicle (EV) manufacturing are not necessarily suitable for the low cost, long-life requirements of renewable applications. Also, LIB fundamentally does not maintain high cycle life in high temperature applications. Also, the risks of thermal runaway also require that LIB maintains a high degree of temperature control, as well as cell-level voltage monitoring and current control. These limitations require the use of LIB in hot climate applications

to include systems with air conditioning, which increases the system complexity, cost, and operating expenses. Since many economic solar applications exist in hot weather climates, the high installed and operating costs of LIB installations limit the penetration of solar in these markets.

[0005] Lead acid battery (LAB) technology is also mature with the key advantages of very low installed costs, and the ability to hold charge for long periods of time. This has resulted in LAB being utilized in many backup power applications, as well as more starting, lighting, and ignition (SLI) applications. The main drawback for LAB is the very limited cycle life tradeoff that exists with the battery depth-of-discharge (DOD). This means that in order to continually cycle LAB for 1000's of cycles, the battery capacity must be substantially oversized to limit the system DOD. This negates the low installed costs. Also, the high temperature tolerance of LAB is generally worse than LIB, which also requires the installation of air conditioning in hot climate applications.

[0006] Aqueous intercalation batteries (AIB) are an emerging battery technology that involves the use of ceramic-based active materials that are capable of ion exchange functionality. Like common LIB cathodes and lithium titanate (LTO) anodes, these materials have transition metals in an inorganic crystal framework. Electrochemical modulation of these metal centers is accompanied by the reversible exchange of mobile cations in order to balance charge. Unlike LIB however, AIB materials operate in a safer, lower cost aqueous electrolyte. But the use of aqueous electrolytes requires the use of lower voltage electrochemical couples, and generally limits the cell voltage of these systems to <2.0V per cell between top-of-charge (TOC) and bottom-of-discharge (BOD). This limits the energy density of these batteries. Therefore, although the active material costs are low, fundamentally durable and temperature tolerant, the low energy density presents a barrier to a cost effective battery. Therefore, AIB must strive for the highest energy density configuration possible in order to meet the required cost targets.

[0007] Among the various ceramic intercalation compounds that have received attention in the literature, the one that has received the most attention is sodium titanium phosphate (STP or NTP). NTP is part of the NASICON family of ceramic compounds, with the general stoichiometry $N_xM_y(PO_4)_z$, where N is preferably an alkali metal and M is a transition metal. For NTP in the discharged state, the typical formulation is $NaTi_2(PO_4)_3$ which intercalates 2 Na^+ ions during charge as the Ti metal centers change

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 simplify 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

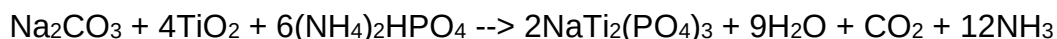
(c) annealing said hollow spheres at 700-900°C to give carbon-coated sodium titanium phosphate hollow spheres, and process B comprises steps (i) mixing a carbon source, a surfactant and part of the precursors of titanium, sodium and phosphate as a wet aqueous mixture; (ii) homogenizing said aqueous mixture 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 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:



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

[0011] To improve the electronic conductivity of the positive electrode 50 % graphite (in weight) is added to the NTP. Both discharged and charged forms of NTP were characterized by XRD and lattice parameters are provided. Bamberger et al.² describe both novel synthesis routes of NTP as well as two other meta-stable phases that involve oxygen incorporation into the Ti centers. The novel synthesis routes involved the use of TiP_2O_7 with either Na_2CO_3 or Na_2HPO_4 as sodium sources to produce the NTP. Other examples in the literature include the "Pechini method" which provides the Ti source as a metal alkoxide in a liquid form³ and the ceramic is produced via a sol-gel route. Although popular in lab investigations, since the NTP can be produced under gentler processing conditions, the cost of the Ti-alkoxide precursor generally precludes this synthesis from industrial consideration. In contrast, it is possible for NTP synthesis through the consolidation of all solid precursors, as in Wu et al.⁴ where ball milling and subsequent microwave thermal annealing of titania, mono-sodium phosphate, di-ammonium phosphate, and graphite was used to generate the carbon-coated NTP. This study also demonstrated the ability for alternate thermal treatments to produce NTP from precursors. Another study provides the means to synthesize NTP by avoiding the use of ammonia-generating species. Phosphoric acid is used with a sodium source to effect the conversion of TiO_xH_y directly to NTP precursor, which is then thermally converted to NTP nano-particles in a Teflon-lined autoclave.⁵

[0012] Several patents that address various aspects of NTP synthesis are worth summarizing. Ukrainian patent UA92887U involves a mechanical melt mixture of polycrystalline materials where a mechanical mixture of NaPO_3 and $(\text{NH}_4)_2\text{HPO}_4$ are ground and melted at 900°C , with the subsequent addition of TiO_2 before crystallization of the NTP product. At least two patent applications (US2018/0358620A1 and US2016/0156035A1) and discuss the fabrication, testing, and benefits of doping the NTP structure with various metals that partially replace the Ti sites as per the general formula $\text{NTi}_{2-x}\text{M}_x(\text{PO}_4)_3$ where M is the doping metal. Generally, the role of the dopants is to improve the cycling stability of the NTP, although it comes at the expense of some degree of specific capacity. US2017/0155130A1 discusses the fabrication of several

² J SOLID STATE CHEMISTRY 73, 317-324 (1988)

³ Journal of The Electrochemical Society, 158 (10) A1067-A1070 (2011)

⁴ Journal of The Electrochemical Society, 160 (3) A497-A504 (2013)

⁵ ACS Sustainable Chem. Eng. 2016, 4, 7074–7079

metal phosphate compounds for battery negative active materials, including NTP, which involves conductive functionality involving graphene, and whose thermal processing may also include microwave treatment.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] Figure 1 shows example recipes for the synthesis of NTP, plus a flowchart of general process steps involved.

[0014] Figure 2 shows the preferred process steps for NTP synthesis using precursors as in Equations 1 & 2.

[0015] Figure 3 shows the preferred process steps for NTP synthesis using precursors as in Equation 3.

[0016] Figure 4 shows particle size distributions of the precursor slurry before and after the addition of carbon black.

[0017] Figure 5 shows a scanning electron microscopy image of the dried precursor powder from the process in Figure 2.

[0018] Figure 6 shows a scanning electron microscopy image of the NTP following pre-cursor powder high-temperature annealing.

[0019] Figure 7 shows an X-ray diffraction pattern of NTP/C powder as produced by the process in Figure 2.

[0020] Figure 8 illustrates the procedure for the NTP leachate analysis.

[0021] Table 1 shows results of NTP leachate analysis of a TiO₂ excess optimization study.

DETAILED DESCRIPTION

[0022] The industrial production of NTP may follow several routes. No matter which route is followed, however, similar production process steps must be followed, which are summarized in a general sense in Figure 1. The NTP precursors that are used must first be homogenized in proper stoichiometric ratios, then consolidated to produce a powder that is amenable for thermal treatment. The homogenization and consolidation steps may employ wet or dry processes, or a combination of the two. Then some form of initial thermal treatment takes place, whose purpose is often to

release by-products of the reactions that would otherwise introduce downstream issues, such as ammonia or water. Then, a long final thermal treatment is used to fully convert the intermediates to the crystalline NTP material. Optionally, a single thermal treatment may replace the two thermal treatments, although this may occur in two stages as described later. Note that conductive carbon, and/or carbon precursors, may be introduced during any or all of the process steps, in order to produce functionally active NTP. In order for the NTP to be functionally active in a battery, it must have adequate electronic conductivity. Since pure NTP has very low electronic conductivity, a conductive carbon coating must be present around NTP particles to make it functionally active as a battery material.

[0023] The process of homogenization involves some form of mixing of the various pre-cursors in proportions related to the stoichiometry of the desired reaction(s). This process may involve wet mixing all of the precursors, which is usually involves water as the homogenization medium. Some of the pre-cursors may be soluble in water and form a solution, while others may be insoluble and form a suspension. In order to increase the stability of the suspension, some form of surfactant may be used. Alternately, if the precursors are available as powders, some form of dry mixing or blending of the powders may occur in the homogenization step. Alternately, the optimal homogenization process may involve the wet mixing of some precursors in water while dry mixing others. This will create two process streams which will require later consolidation. Note that any wet mixing that occurs in the homogenization step will require a sub-sequent consolidation step, as described next.

[0024] The process of consolidation will involve bringing the precursors together into intimate contact to result in a powder that is amenable for the sub-sequent thermal treatment steps. When an aqueous homogenization process was used, then some form of water removal must occur. Although many forms of drying are available, spray drying is most commonly employed. This process affords some degree of control over the resulting particle size distribution of the powder, including the online segregation of very fine particles, which can benefit the downstream thermal processing. Prior to thermal processing, there may be inserted additional process steps in order to further optimize the properties of the powder, include additional batch drying, grinding, and / or particle size classification.

[0025] The thermal treatment of the NTP precursors may be carried out using a single step, or two steps, either using batch or continuous processing. Single-step batch processing may include the use of static ovens into which are loaded ceramic or graphite crucibles containing the homogenized & consolidated precursors. The initial thermal treatment may occur to a preliminary stage, where thermal decomposition by-products are released as gaseous emissions. The partially treated precursor powder is then moved to a final thermal process. Some optional degree of grinding and carbon addition may occur in this during this interim step. Or, a static furnace may be used to perform the entire thermal treatment operation in a single step. However, it is common that even if the precursors are only loaded into the oven once, there are usually multiple temperatures in the thermal treatment program that are used. As above, the initial thermal treatment usually occurs to remove the bulk of gaseous by-products, followed by a final treatment, which performs the full conversion to the crystalline NTP material. If there are two discrete thermal processing steps, there may be inserted additional steps in between these to optimize the powder properties, include additional grinding and / or particle size classification.

[0026] Either in combination with the above or in isolation, continuous forms of thermal treatment may also be employed. These include rotary kilns, elevator kilns, or belt furnaces. Each of these methods perform the thermal treatment in a continuous manner, although trade-offs exist for each. While rotary kilns may be the least expensive means of thermal treatment on a per-kg basis, the complexity of the operation may not result in the optimal thermal treatment. This is because of their relatively low residence times, and the complex relationship between operating temperature, residence time, and rheology of the powder. In contrast, elevator kilns and belt furnaces utilize very long heating zones to effect very long residence times at various temperatures. This allows these methods to very accurately administer specific temperatures and times to the material. However, they also require comparatively high capital expenditures, large footprints, high power consumption, and use of high rates of inerting gases. Note that all of the thermal treatment of NTP at all stages usually occurs in the absence of oxygen, which is usually achieved by some combination of vacuum treatment or inert gas purging. These continuous means of thermal processing are usually justified at suitably high rates of production.

[0027] As seen earlier, microwave treatment may be utilized as a form of thermal treatment, either in a batch or continuous process. Lab-scale studies have shown that microwave processing can provide uniform heating of NTP precursors, and if implemented at the industrial scale, may result in significantly reduced processing times (~1 hr) and energy consumption have also been demonstrated at lab scale. Challenges include the large differences in microwave susceptibility of the different precursors, and the resulting non-uniform thermal profile within the powder. Optimizing microwave processing for NTP production requires optimizing the effects of the microwave cavity and frequency, the use of additives to appropriately increase or decrease the precursor microwave susceptibility, and the possible combination of conventional + microwave, or hybrid, thermal treatments.

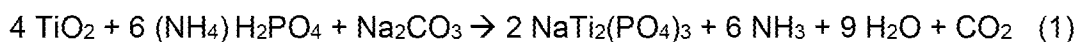
[0028] In order to produce NTP, the precursor chemicals must include some form of sodium, titanium, and phosphate. Although many potential forms of pre-cursors exist for each of these, those disclosed here are of industrial interest due to their low cost and/or favorable processing characteristics. For sodium, favorable precursors include sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3). For phosphate, favorable precursors include one or more of the sodium phosphates (Na_3PO_4 , Na_2HPO_4 , NaH_2PO_4), phosphoric acid (H_3PO_4), and/or one or more of the ammonium phosphates ($(\text{NH}_4)_3\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, $\text{NH}_4\text{H}_2\text{PO}_4$).

[0029] Precursor sources of titanium may include any compound of Ti(IV), including TiO_2 , $\text{Ti}(\text{OH})_4$, or TiCl_4 . While these Ti precursors represent sources of only Ti, other compounds may include other required precursor constituents. For example, $\text{Ti}_3(\text{PO}_4)_4$ is a precursor wherein at least some of the required phosphate is already included. Another example includes $\text{C}_{16}\text{H}_{36}\text{O}_4\text{Ti}$ (tetrabutyl titanate) which will hydrolyze in water to form $\text{TiO}(\text{OH})_2$. In this latter example, at least some of the required carbon for the conductive coating can be provided. In these latter two examples, the higher cost of these titanium precursors may be justified if adequate simplification of downstream processes occur.

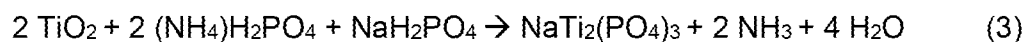
[0030] If adequate carbon is not provided as part of the precursors, then some form(s) of carbon must be introduced into the processing in order for the NTP particles to be functionalized with a conductive coating. Various options exist for the forms of carbon that are used, including both soluble and insoluble forms of carbon or carbon

precursor. Insoluble forms include high surface area carbon black, graphite, graphene, or carbon nanotubes. Soluble carbon precursors include various forms of sugar, such as sucrose, which is usually used when some form of wet consolidation of precursors is used. Ideally, these sugars are intimately incorporated into the other precursors and, when thermally treated in the downstream processing, are converted to elemental carbon to aid in increasing the NTP electronic conductivity.

[0031] Several types of the aforementioned precursors may be combined to form NTP. Although various types of precursors may be utilized, the following summarizes those of greatest industrial significance, the main reason being that the cost of the precursors is low for all of these methods. One popular method, represented by Equations 1 & 2, is the use of titanium dioxide powder, either of di-hydrogen ammonium phosphate and/or di-ammonium hydrogen phosphate, and sodium bicarbonate. Both of these methods are very similar, with (1) being slightly preferable due to the lower amount of ammonia emitted.



[0032] Another method that further reduces the emissions involves combining the titanium dioxide with di-hydrogen ammonium phosphate and di-hydrogen sodium phosphate, as shown in Equation 3. Although the precursors are slightly more expensive, the combination of combining the sodium and phosphate sources in a single precursor without needing to emit carbon dioxide may provide processing benefits that offset the added costs.



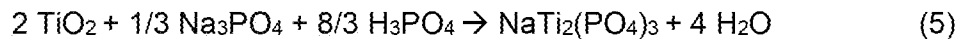
[0033] These previous 3 methods all involve the emission of ammonia at some point in the process. Typically, ammonia is emitted in either of the initial or final thermal treatment steps, depending on the type of thermal processing used. This must be swept out of the equipment by high rates of inert gases to minimize furnace corrosion at the high temperatures involved. These gases must then be treated further by scrubbing and neutralization to comply with the applicable air and water emissions standards.

[0034] These complications make the production of NTP without the emission of ammonia highly desirable. Several methods involve the combination of titanium pre-

cursor, sodium pre-cursor, and phosphoric acid to result in a more direct formation of NTP. One method involves the direct formation of NTP from titanium hydroxide, sodium hydroxide, and phosphoric acid⁵.

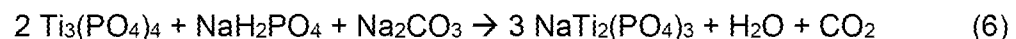


Another method capable of this involves the direct formation of NTP from combining titanium dioxide with sodium phosphate and phosphoric acid:



Although these example methods avoid the ammonia formation, the use of phosphoric acid as a precursor places cost and design constraints on the capital used for precursor consolidation and homogenization, such as the need for Telfon-coated equipment to prevent the corrosion and contamination of harmful metals into the NTP.

[0035] Other methods exist to produce NTP without the formation of ammonia. One involves the reaction of $\text{Ti}_3(\text{PO}_4)_4$ to produce NTP as:



Unlike the previous examples, phosphoric acid is not used and this method will avoid the need for highly corrosion-resistance processing equipment. However, this advantage comes with the disadvantage of the higher precursor cost of $\text{Ti}_3(\text{PO}_4)_4$.

[0036] Although there are many potential combinations of homogenization, consolidation, and thermal treatments that are possible, some preferred means of industrial processing can be illustrated for various precursor combinations. Figure 2 illustrates an example process for NTP synthesis using precursors in Equations 1 & 2. The various required precursors (titanium dioxide powder, di-ammonium hydrogen phosphate, and sodium carbonate) are combined with conductive carbon additives (both insoluble carbon black, and optional soluble sucrose) and water into a mix tank. The contents are thoroughly mixed with the soluble precursors dissolved in the water while the insoluble species are suspended in a slurry. Optionally, a polymer surfactant may be used to improve the stability of the mixture. Following adequate mixing time, the slurry is fed to a spray dryer where the water is evaporated, leaving a homogenized powder that is amenable for thermal processing. This step may occur via batch ovens or continuous belt furnaces with various time-temperature programs to maximize the product quality and minimize the contaminating effects of gaseous by-products.

[0037] Figure 3 illustrates an example process for NTP synthesis using precursors in Equation 3. The initial process step involves the wet consolidation of the precursors. This may occur in a similar fashion to Figure 2 using a mix tank with water, or may occur in a wet attritor mill with water and media (e.g., zirconia beads) in order to break down the agglomerates during consolidation. This combination of precursors may be somewhat advantaged over Equations 1 & 2 due to the lack of the sodium carbonate precursor, which may complicate the process with the liberation of carbon dioxide. Next, a drying step occurs, which may involve spray drying as previously discussed, or tray drying in order to remove the water and leave behind the consolidated precursors. The next steps involve a thermal decomposition step where the ammonia gas is liberated from the mixture at a suitable temperature, prior to an intermediate milling step prior to the calcining operation where a suitably high temperature converts the precursors to the crystalline NTP with intimate carbon functionalization. The final step involves screening to remove extremely large or small particles that would introduce problems in later electrode processing before packaging. As shown in Figure 3, there is the option to avoid the intermediate thermal decomposition step and perform the entire thermal processing in a single step, as was shown in Figure 2.

[0038] Both during and following NTP synthesis, there are key analytical methods that are used to assess the material quality. These include particle size distribution (PSD), X-ray diffraction (XRD), scanning electron microscopy (SEM), carbon content analysis, and a pH/ conductivity test. These tests occur at various steps during the NTP synthesis and, in some cases, gate the further processing steps by achieving certain quality metrics.

[0039] Figure 4 shows particle size analysis from the precursor slurry during the wet mixing step of Figure 2. The effect of the carbon addition is to shift the average particle size higher. In Figure 2, the precursors are listed in order of addition, so that the carbon sources (both soluble and insoluble) occur last. This is to allow intimate contact of the NTP precursors prior to the introduction of carbon, since the ideal structure of the resulting NTP is that of NTP crystallites surrounded by conductive carbon. The optimal carbon content will sufficiently reduce the electronic resistivity in the product powder without significantly reducing its specific capacity.

[0040] Following drying, samples of the resulting precursor powder are analyzed by SEM to assess particle size and morphology. Figure 5 shows an example SEM image of precursor powder generated following the spray drying process in Figure 2. Typical particle sizes from this operating are $\sim 50\mu\text{m}$, with some finer particles that were not removed from the cyclone separator. Depending on the operating parameters of the spray dry tower, the resulting powder that will progress onto thermal processing may or may not include the finer particles that are captured from the cyclone separator.

[0041] As discussed earlier, a high temperature thermal treatment is required to convert the precursors into the crystalline NTP material. Whether occurring in either separate or unified decomposition & annealing operations that operate in either batch or continuous modes, the time / temperature regimes that are used must be carefully chosen. These conditions must balance the difficult trade-offs that exist to preserve the carbon network within the NTP precursor material. Under-annealing at too low a temperature results in under-conversion of the NTP precursors and leads to significant issues in the subsequent battery operation. Over-annealing at too high a temperature leads to the attendant carbon acting as a reductant and a re-conversion of the NTP crystalline phase. The loss of this network carbon can lead to accelerated capacity fade during battery operation. In order to manage these tradeoffs, annealing occurs for long durations in order to completely convert the NTP precursors with minimal consumption of the network carbon. These include roughly 2-4 hours of an initial thermal treatment at 200-300 °C in order to remove gaseous by products, followed by 8-12 hours of 700-900 °C in order to complete the conversion to crystalline NTP.

[0042] Figure 6 shows example SEM images of the resulting crystalline NTP functionalized with carbon. In general, a slight reduction of the average particle size is seen, along with some slight variation in contrast due to non-uniformity of the carbon coating. Analysis for the amounts of carbon present in the sample is performed by measuring the weight loss after a 4hr sintering in air at 900 °C. Desirable mass % of carbon in properly synthesized NTP/C is around 14-18%. The presence of crystalline NTP is confirmed by XRD as shown in Figure 7, where nearly all of the major peaks are indicative of NTP. Others that are visible include graphite from the carbon source, and a slight presence of excess TiO_2 . The peak positions for TiP_2O_7 , which is usually an indication of under-annealing, are also shown although no peaks are present in this sample.

[0043] Another analytical technique that is used to assess the degree of precursor conversion involves a leaching with hot de-ionized water, followed by various analyses of the leachate. This procedure is illustrated in Figure 8. Typical analyses that are performed on the leachate can include either a simple pH / conductivity assessment, or analyses for specific constituents. Typical pH values for properly synthesized NTP/C are in the range of 3-7, and a conductivity reading of $<600\mu\text{S/cm}$. Analysis for specific elements can assist in optimizing the production recipe. Table 1 shows the results of a study optimizing the amount of TiO_2 excess in the precursor recipe using the process in Figure 2. The results indicate that 2% by wt. excess TiO_2 minimizes both the conductivity and the amounts of leachable elements.

Table 1

TiO_2 wt% excess	pH	σ (S/cm)	Na (mg/L)	P (mg/L)	Ti (mg/L)
0%	4.918	713	128.3	213.2	5.139
2%	5.369	294	51.55	68.86	0.938
4%	6.708	378	82.89	74.41	1.388
6%	5.338	432	87.79	125.4	4.151

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°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 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 $4 \text{TiO}_2 + 6 (\text{NH}_4) \text{H}_2\text{PO}_4 + \text{Na}_2\text{CO}_3 \rightarrow 2 \text{NaTi}_2(\text{PO}_4)_3 + 6 \text{NH}_3 + 9 \text{H}_2\text{O} + \text{CO}_2$.

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 $4 \text{TiO}_2 + 6 (\text{NH}_4)_2\text{HPO}_4 + \text{Na}_2\text{CO}_3 \rightarrow 2 \text{NaTi}_2(\text{PO}_4)_3 + 12 \text{NH}_3 + 9 \text{H}_2\text{O} + \text{CO}_2$.

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 $2 \text{TiO}_2 + 2 (\text{NH}_4)\text{H}_2\text{PO}_4 + \text{NaH}_2\text{PO}_4 \rightarrow \text{NaTi}_2(\text{PO}_4)_3 + 2 \text{NH}_3 + 4 \text{H}_2\text{O}$.

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 $2 \text{TiO}_2 + 1/3 \text{Na}_3\text{PO}_4 + 8/3 \text{H}_3\text{PO}_4 \rightarrow \text{NaTi}_2(\text{PO}_4)_3 + 4 \text{H}_2\text{O}$.

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 $2 \text{Ti}_3(\text{PO}_4)_4 + \text{NaH}_2\text{PO}_4 + \text{Na}_2\text{CO}_3 \rightarrow 3 \text{NaTi}_2(\text{PO}_4)_3 + \text{H}_2\text{O} + \text{CO}_2$.

7. The method of claim 1, wherein precursors of titanium are selected from TiO_2 , $\text{Ti}(\text{OH})_4$ and $\text{Ti}_3(\text{PO}_4)_4$.

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.