



# Preparation and application of a titanium dioxide/graphene oxide anode material for lithium–ion batteries



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## HIGHLIGHTS

- Paper describes properties of anode based on titania and graphene oxide.
- It has been showed some physicochemical properties of the TiO<sub>2</sub> nad TA/GO.
- TA/GO was prepared via hydrothermal method nad TiO<sub>2</sub> – via sol–gel method.
- It has shown that capacity of the TA/GO depends on the current rate.
- The TA/GO|Li system exhibits a long-life of more than 50 cycles.

## ARTICLE INFO

### Article history:

Received 12 June 2015

Received in revised form

14 August 2015

Accepted 3 September 2015

Available online xxx

### Keywords:

TiO<sub>2</sub>

Graphene oxide

Cyclability

Chemically-bonded

Li–ion battery

## ABSTRACT

This paper describes the synthesis and physicochemical properties of a new type of titania/graphene oxide (TA/GO) composite. Titania powder was synthesized via the sol–gel method, and its surface was functionalized with *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (AAPTMS) to increase its adhesion to graphene oxide. Transmission electron microscopy (TEM), non-invasive back scattering (NIBS), porous structure parameters (low-temperature nitrogen sorption), degree of modification of titania and TA/GO determined by Fourier-transform infrared spectroscopy (FT-IR), impedance analysis, charging/discharging and cyclic voltammetry were carried out.

At a current density of 50 mA g<sup>-1</sup>, the good cyclability exhibited by the TA/GO anode can be readily retained at 370 mAh g<sup>-1</sup> after 50 cycles, which is outstanding among the TiO<sub>2</sub> composites reported in the literature.

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## 1. Introduction

Titanium dioxide (TiO<sub>2</sub> or titania) has been extensively investigated as an anode material for Li–ion batteries (LIBs) due to its high-rate lithium storage and high packing density [1]. It appears to be an alternative to classical graphite-based anodes, because of its excellent electrochemical performance, cheapness and low toxicity [2–4]. TiO<sub>2</sub> has been paid much attention as an anode material for LIBs because it operates in a voltage range of 1.6–1.9 V vs. Li/Li accompanied by insertion and extraction of Li ions [5]. These characteristics render it a potential anode material for high-power lithium ion batteries, avoiding the need for a passivation layer at

the contact with the liquid electrolyte [5–8].

Interestingly, TiO<sub>2</sub> has various polymorphs such as rutile [9], brookite [10], anatase [11–13], TiO<sub>2</sub>(B) [14], etc. Under standard conditions, rutile is the thermodynamically most stable structure of TiO<sub>2</sub>, and is also the most common natural form [15]. Nano-structured anatase TiO<sub>2</sub> materials are considered promising for high-rate Li storage because of their large specific surface area and suitable structure for lithium intercalation [16–21]. TiO<sub>2</sub>(B) has a more open structure than rutile, anatase or brookite, with significant voids and continuous channels that are capable of intercalation [22].

TiO<sub>2</sub> polymorphs, typically anatase, rutile and brookite, are characterized by a relatively high theoretical capacity (335 mAh g<sup>-1</sup>, as regards the intercalation of 1 Li<sup>+</sup> per TiO<sub>2</sub>, which is close to the 372 mAh g<sup>-1</sup> for graphite), negligible lattice changes during Li ion insertion/extraction (<4% for anatase), and a lithium

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ion insertion/deinsertion potential range vs.  $\text{Li}^+/\text{Li}$ . Hence the material is inherently safer than graphite, avoiding Li electroplating and making the formation of a solid–electrolyte interface unlikely [23,24]. The main disadvantage arising from the high  $\text{Li}^+$  insertion/deinsertion potential of  $\text{TiO}_2$  is that it lowers the overall cell working potential with respect to graphite when coupled with the same cathode [25]. Generally,  $\text{TiO}_2$  anatase can reversibly uptake 0.5  $\text{Li}^+$  per formula unit through a biphasic mechanism which comprises the Li-poor tetragonal  $\text{Li}_{0.05}\text{TiO}_2$  and the Li-rich orthorhombic  $\text{Li}_{0.5}\text{TiO}_2$  [26], leading to a theoretical capacity of 167  $\text{mAh g}^{-1}$ . On the other hand, rutile and brookite are able to accommodate only small numbers of lithium ions [2,27–30]. Anatase is a typical insertion material: almost half of its available interstitial octahedral sites can be randomly occupied by  $\text{Li}^+$  ions [1], and thus its electrochemistry is largely particle-size-dependent [31]. Hence its electrochemical properties (such as specific energy, storage capacity, high-current discharge/charge ability and cycling stability) can be improved by nanostructuring the electrodes [32–34]. Indeed, those compounds that in bulk form possess low Li diffusion coefficients usually exhibit low lithium ion storage capacities at high-current regimes [35].

This paper reports on the synthesis, electrochemical properties and performance of microsize spherical  $\text{TiO}_2$  and TA/GO secondary particles applied as a new anode materials in lithium ion batteries.

## 2. Experimental

### 2.1. Materials

Titanium tetraisopropoxide (TTIP, 97%), *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane (AAPTS, 97%) and graphene oxide (GO, 2  $\text{mg}\cdot\text{mL}^{-1}$ , dispersion in water) were purchased from Sigma–Aldrich. Ammonia (25%), propan-2-ol (IPA, 99.5%), methanol (MeOH, 99.8%) and ethanol (EtOH, 99.8%) were purchased from Chempur (Poland). All reagents were used without any further purification.

Graphite (G, SL-20, BET surface area 6.0  $\text{m}^2 \text{g}^{-1}$ , Superior Graphite, USA), carbon black (CB, Fluka), poly(vinylidene fluoride) (PVdF,  $M_w = 180\,000$  Fluka), lithium foil (Aldrich, 0.75 mm thick), vinylene carbonate (VC, Aldrich), *N*-methyl-2-pyrrolidinone (NMP, Fluka), lithium hexafluorophosphate ( $\text{LiPF}_6$ , Aldrich), ethylene carbonate (EC, Fluka) and dimethyl carbonate (DMC, Fluka) were used as received.

### 2.2. Synthesis of titania via the sol–gel method and its surface modification

Titania powder was synthesized via the sol–gel method, in a slightly modified form from that described previously by the authors [36]. First, an appropriate amount of the titania precursor TTIP was dissolved in propan-2-ol at room temperature. The whole mixture was placed in a conical flask to which ammonia – the catalyst for hydrolysis – was introduced at a constant rate of 2  $\text{mL min}^{-1}$  using an ISM833A peristaltic pump (Ismatec). The initially clear solution turned into a white dispersion. The resulting mixture was vigorously stirred for 1 h using a high-speed stirrer of T25 Basic type (IKA Werke GmbH), operating at 1200 rpm. After that time the entire system was placed in an SEL-13 chamber drier (Mettler) at 105 °C for 18 h. The resulting alcogel was washed repeatedly with deionized water and filtrated to remove residual solvent and catalyst. At the final stage, the sample was dried at 105 °C for 6 h, and then calcined at 600 °C for 2 h (Nabertherm type Controller P320).

To increase the adhesion of titania to graphene oxide, its surface was functionalized with AAPTS. Modification was performed using

1 wt./wt. of AAPTS (calculated for 100 g of titania) prepared in a methanol/water mixture (4/1 v/v), and applying the so-called dry technique, described in detail in Refs. [37,38]. This modification resulted in a powder material with positively charged surface, which enables its strong interaction with negatively charged GO.

### 2.3. Synthesis of titania/graphene oxide hybrid material

The titania/graphene oxide hybrid material (TA/GO) was prepared via a hydrothermal method. First, 5 mL of GO suspension (2  $\text{mg}\cdot\text{mL}^{-1}$ ) was added to 20 mL of aqueous dispersion of aminofunctionalized  $\text{TiO}_2$  (100  $\text{mg}\cdot\text{mL}^{-1}$ ) and sonified. After 15 min of sonification the mixture was centrifuged at 4000 rpm for 20 min (Centrifuge 5810 R, Eppendorf). Then the wet TA/GO powder was dispersed in a deionized water/ethanol mixture (1/1 v/v), placed in a Teflon-lined stainless steel reactor and thermally treated (120 °C for 4 h), after which it was naturally cooled to room temperature. The resulting grey precipitate was filtered, washed with deionized water and dried at 60 °C for 2 h.

### 2.4. Preparation of electrolyte and electrode

Electrolytes were obtained by dissolution of the  $\text{LiPF}_6$  solid salt in liquid EC/DMC (1:1).

The tested anodes were prepared on a copper foil (Hohsen, Japan) using a casting technique, from a slurry of  $\text{TiO}_2$ /graphene oxide, carbon black and PVdF in NMP. The ratio of components was TA/GO:AB:PVdF = 75:15:10 (by weight). After evaporation of the solvent (NMP) at 120 °C in vacuum, a layer of the TA/GO electrode containing the acetylene black (AB) and binder (PVdF) was formed. The electrode typically contained 2.5–3.5 mg of TA/GO.

### 2.5. Procedures and measurements

The dispersive properties of the materials obtained were evaluated based on the non-invasive back scattering technique (NIBS) using a Zetasizer Nano ZS (Malvern Instruments Ltd.). The morphology and microstructure of the  $\text{TiO}_2$  (sample T) and  $\text{TiO}_2/\text{GO}$  (sample TA/GO) materials were observed using a Jeol 1200 EX II transmission electron microscope, operating at an accelerating voltage of 100 kV. An ASAP 2020 porosimetry analyzer (Micromeritics Instrument Co.) was used to determine parameters of the porous structure of the  $\text{TiO}_2$ -based materials, including surface area (BET model), pore size and pore volume. The instrument operates based on low-temperature sorption of  $\text{N}_2$ . The X-ray diffraction method (XRD) was used to determine and identify any crystalline phases in the synthesized powder materials. XRD analysis was performed using a TUR-M62 diffractometer with  $\text{Cu K}\alpha$  radiation ( $\alpha = 1.5418 \text{ \AA}$ ), Ni filtered. The patterns were obtained in step-scanning mode ( $\Delta 2\theta = 0.04^\circ$ ) over an angular range of 10–80°. To identify the characteristic groups present on the surface of the materials, the samples underwent FT-IR analysis using an IFS 66v/s spectrophotometer (Bruker). The samples were studied in the form of KBr tablets, over a wavenumber range of 4000–400  $\text{cm}^{-1}$ .

The electrochemical properties of the cells were determined by electrochemical impedance spectroscopy (EIS) and galvanostatic charging/discharging tests. The cycling measurements were taken with the use of the ATLAS 0461 MBI multichannel electrochemical system (Atlas-Sollich, Poland) at different current density. Charging/discharging measurements were carried out at 25 °C. Cyclic voltammetry (CV) and AC impedance measurements were performed using the  $\mu$ Autolab FRA2 type III electrochemical system (Ecochemie, Netherlands).

Electrodes were separated by the glass microfiber GF/A separator (Whatmann, 0.4–0.6 mm thick), placed in an adapted

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