



# Electrochemical properties of nanocrystalline TiO<sub>2</sub> synthesized via mechanochemical reaction

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## ABSTRACT

Nanocrystalline anatase TiO<sub>2</sub> is successfully synthesized via a facile and rapid mechanochemical reaction with subsequent annealing in different atmospheres. Transmission electron microscopy observation and X-ray diffraction peak broadening reveal the average crystallite size to be about 11 nm. Cyclic voltammetry and galvanostatic discharge–charge tests at various current densities are carried out to explore electrochemical properties of the synthesized materials. The first discharge and charge capacities can reach 325 mAh g<sup>-1</sup> and 234 mAh g<sup>-1</sup>, respectively. Moreover, nanocrystalline TiO<sub>2</sub> also exhibits good rate capability and excellent capacity retention for over 700 cycles.

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## 1. Introduction

Lithium-ion battery (LIB) has been gradually adopted for large-scale applications such as hybrid/electric vehicles (HEVs/EVs) and electric grids [1–3]. Therefore, development of fast charge and safe LIBs is critical to achieve zero emission all-electric vehicles in the next decade. This development is dependent on both cathode and anode materials. Traditional graphite carbon has been used as anode since the LIB was first commercialized in 1991. However, flammability of lithiated graphite and metallic lithium plating upon fast charge are severe risks in large scale multi-cell systems [4]. Hence, many efforts have been devoted to alternatives such as TiO<sub>2</sub>/Li<sub>x</sub>TiO<sub>y</sub>, tin and silicon.

Among various candidates for anode materials, titanium based materials, especially TiO<sub>2</sub> and Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub>, have received particular attention for their crucial advantages in safety features. Li<sup>+</sup> insertion potential for Ti<sup>3+</sup>/Ti<sup>4+</sup> redox is normally ~1.5–2 V, well lying inside organic electrolyte window (1–4.8 V) [5]. Titanium based materials also undergo much smaller volume changes upon lithiation (e.g. 4% for anatase TiO<sub>2</sub>) than graphite (10%), Sn and Si (>300%), leading to better electrode stability [6,7]. TiO<sub>2</sub> has a much higher theoretical capacity (335 mAh g<sup>-1</sup>) as compared to Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (175 mAh g<sup>-1</sup>), though it is still challenging to reversibly utilize the theoretical capacity. Li<sup>+</sup> insertion in bulk TiO<sub>2</sub> is hindered by wide band gap in nature and poor Li<sup>+</sup> transport. Nano-sizing is therefore necessary to improve Li<sup>+</sup> insertion behavior by shortening

diffusion distances and enlarging electrode/electrolyte contact area [8,9]. In previous studies, nano-sized TiO<sub>2</sub> was commonly synthesized via hydrolysis or hydrothermal reaction [8–14]. In this work, nanocrystalline anatase TiO<sub>2</sub> was synthesized via mechanochemical reaction, which is a rapid, facile and economic process [15–19]. It has been successfully used to synthesize nanostructure rutile TiO<sub>2</sub> reinforced Sn [20], while we report here its first application for synthesis of pure anatase TiO<sub>2</sub> as active anode material.

## 2. Experimental

### 2.1. Material preparation

Mechanochemical reaction between titanium chloride (TiCl<sub>4</sub>) and ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>) was induced by high-energy milling in an inert atmosphere. In a typical process, liquid TiCl<sub>4</sub> (99%, Sigma–Aldrich) and NH<sub>4</sub>HCO<sub>3</sub> (99%, Merck) were sealed in a stainless steel mill jar inside an argon glove box (MBraun; H<sub>2</sub>O, O<sub>2</sub>: <0.1 ppm). Then, high-energy ball mill was carried out for 15 min using SPEX-8000M. Finally, the as-milled powders were annealed at 400 °C, 500 °C, 600 °C and 700 °C for 1 h in air and flowing argon, respectively. The synthesized TiO<sub>2</sub> materials were denoted shortly by annealing conditions.

### 2.2. Characterization

Crystal structure was characterized by X-ray diffraction (XRD, Shimadzu XRD-7000, Cu-Kα radiation) with a step width of 0.02° and a scan rate of 1°/min. In addition, high counts XRD data were acquired between 23° and 28° (2θ) with slow step scan of 12 s

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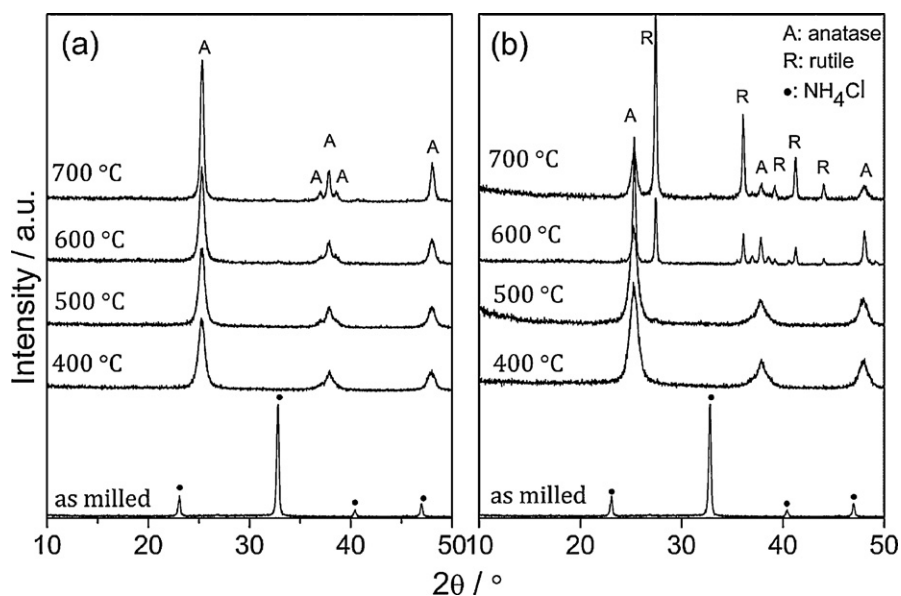


Fig. 1. XRD patterns of the milled precursor and TiO<sub>2</sub> annealed (a) in air and (b) in argon.

per step (0.1°/min). Micromorphology was observed by scanning electron microscope (SEM, Hitachi S-4300) and transmission electron microscope (TEM, JEM2010F). Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the as-milled powder were conducted by Shimadzu DTG-60H up to 1000 °C with 10 °C/min heating rate. Electronic conductivity was measured by direct current (DC) polarization method using Solartron 1287+1260 electrochemistry system. A DC polarization 0.5 V was applied to the compacted powders within a Swagelok-type cell for 1 h until a stationary current was reached.

### 2.3. Electrochemical test

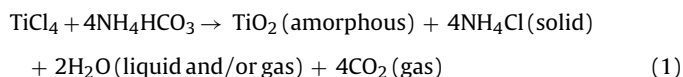
Electrochemical investigations of the synthesized TiO<sub>2</sub> were carried out using two electrode half-cells with metallic lithium foil as counter and reference electrode. To fabricate TiO<sub>2</sub> working electrodes, 80 wt.% active material, 15 wt.% carbon black (Super P™) and 5 wt.% polyvinylidene fluoride (PVDF, 99%, Sigma–Aldrich) binder were thoroughly mixed in *n*-methyl-2-pyrrolidone (NMP) to obtain a homogenous slurry. The viscous slurry was then pasted on a copper foil by doctor-blade method. The prepared electrodes with active loading density of 3–4 mg cm<sup>-2</sup> were thoroughly dried in a vacuum oven at 120 °C for 12 h and rolled by a rolling machine. The half cells were assembled using Swagelok type cells in an argon glove box. One Celgard 2500 separator was sandwiched by a TiO<sub>2</sub> working electrode and a 0.59 mm thick metallic lithium foil. 1 M LiPF<sub>6</sub> in ethylene carbonate, diethyl carbonate and dimethyl carbonate (EC:DEC:DMC, 1:1:1 in volume) solutions was used as the electrolyte. Galvanostatic discharge–charge cycling tests were carried out between 1.0 V and 3.0 V using Maccor 4304 or Neware BTS-5V1A at room temperature (24 °C). Cyclic voltammetry (CV) measurement was carried out at a scan rate of 0.1 mV s<sup>-1</sup> using Solartron 1400 cell system.

## 3. Results and discussion

### 3.1. Crystal structure

Fig. 1 shows XRD patterns of the investigated materials. After milling, NH<sub>4</sub>Cl is the only detectable phase in the as-milled powders, while the TiO<sub>2</sub> could be in an amorphous form. Therefore, the

overall mechanochemical reaction upon ball mill can be expressed as:



After annealing, diffraction peaks from NH<sub>4</sub>Cl vanish, whereas crystallized anatase and rutile become the only remaining phases depending on annealing temperature. Crystal structures of the annealed TiO<sub>2</sub> vary with annealing atmosphere. For TiO<sub>2</sub> annealed in air, single-phase anatase was obtained starting from 400 °C to 700 °C. On the other hand, for TiO<sub>2</sub> annealed in argon, single-phase anatase was obtained at 400 °C and 500 °C, while rutile started to emerge at 600 °C and became the main phase at 700 °C. Anatase–rutile phase transition temperature is clearly lowered below 600 °C in a non-oxidizing atmosphere.

Average crystallite size was estimated from XRD peak broadening by application of Scherrer equation [21,22]. Fig. 2 shows high counts XRD pattern of single-phase anatase TiO<sub>2</sub> collected between 23° and 28° (2θ). The full-width at half maximum (FWHM) of the anatase (101) peak at 25.3° was measured.  $K_{\alpha 2}$  contributions were subtracted by software, while instrumental broadening

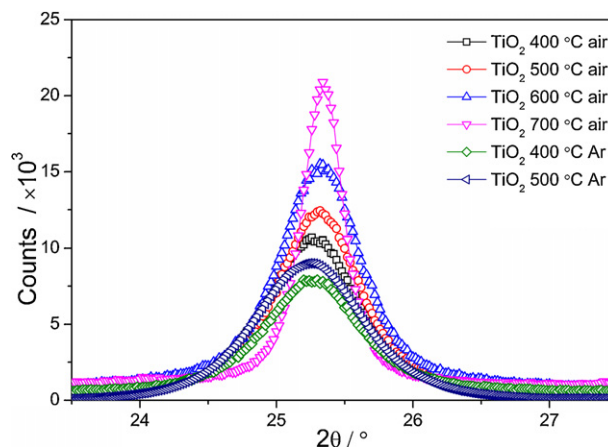


Fig. 2. High counts XRD patterns of anatase (101) peak.

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