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High power layered titanate nano-sheets as pseudocapacitive lithium-ion battery anodes

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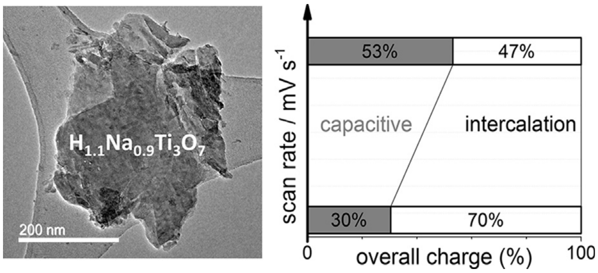
HIGHLIGHTS

- Layered titanates with high surface area are synthesized *via* CHFS.
- The as-prepared nano-sheets can be used as the active component in the electrode.
- The high power performance remains excellent for current rates up to 10 A g^{-1}.
- The charge is stored *via* pseudocapacitance intercalation.

GRAPHICAL ABSTRACT



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ABSTRACT

Ultra-thin layered sodium titanate nano-sheets were synthesised using a continuous hydrothermal flow process and the as-prepared materials were investigated as an anode material for lithium-ion batteries. In comparison to previous studies on similar materials, the layered titanates herein showed high electrochemical activity at lower potentials. Cyclic voltammetry measurements in the potential range of 0.05 −2.1 V *vs.* Li/Li^+, revealed that charge storage occurred from both lithium-ion intercalation as well as pseudocapacitive surface chemical processes. During electrochemical cycling tests, a high specific current of 0.5 A g^{-1} was applied and the cells achieved a stable specific capacity of *ca.* 120 mAh g^{-1} for over 1200 cycles. Even at an applied current of 10 A g^{-1}, the electrode material delivered a stable specific capacity of 38 mAh g^{-1}, which suggests that this material may be suitable for high power applications.

1. Introduction

Rechargeable lithium-ion batteries are an important technology for energy storage, with applications ranging from consumer electronics to electric vehicles. A lithium-ion battery typically consists of an anode and a cathode, which are kept apart by a separator, which is soaked in an electrolyte containing lithium-ions [1]. There are currently numerous candidates for the development of lithium-ion battery anodes, which include insertion/intercalation materials, alloying materials and conversion materials [2–4]. In particular, insertion/intercalation electrodes have the ability to

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delithiate/lithiate the crystal structures *via* n-dimensional channels (where n = 1– 3). Titania based materials are of specific interest because they are inexpensive, sustainable, environmentally friendly, thermally stable, and very safe when used as electrodes in lithium-ion batteries [4]. Furthermore, titanium-based materials have shown reasonable specific capacity (*e.g.* $TiO_2 = 335$ mAh g^{-1} and $Li_4Ti_5O_{12}$ (LTO) = 175 mAh g^{-1}) [5], low irreversible capacity loss during the first cycles, high power capability and a very high cycle life, due to minimal volume and structural change in the material during cycling. However, many of these titanium-based anodes have a narrow operational potential window, which can substantially limit the specific energy of a cell, limiting the utility of these materials in certain applications [6,7].

Graphite is the most commonly used intercalation anode material in lithium-ion batteries. It is relatively inexpensive, has a high specific theoretical capacity of 372 mAh g^{-1} and operates at relatively low potentials (range of 0.3–0.1 V *vs* Li/Li^+). However, formation of a solid electrolyte interface (SEI) at the surface is necessary to stabilise the anode (but this leads to a large loss of capacity on the first cycle), and another drawback includes poor rate retention at applied currents >10 C [8–11]. Due to kinetic limitations during the intercalation of lithium-ions between the graphene layers [12], graphite can suffer in terms of safety, *e.g.* lithium plating and dendrites can be formed, which can lead to short circuits [13].

Layered titanates possess a very large interlayer spacing (*ca.* 0.8 nm, compared to graphite, *ca.* 0.34 nm) and can be used as anodes in high power lithium-ion batteries [14,15]. By making nanosized layered anode materials, it may be possible to improve the kinetics of lithium-ion intercalation/deintercalation, by greater access of the ions to the channels as a result of increased surface area to volume ratio. Recently, it has been shown that a high surface area can drastically enhance the amount of stored charge [16]. This is a result of a shift from a battery-like behaviour to oxide supercapacitor-like behaviour, as the stored charge arises more from surface effects such as fast pseudocapacitive faradaic reactions [17].

The academic literature contains a number of preparative methods for nanosized electrode materials, including solid state syntheses [18], flame syntheses [19,20], pyrolysis [21], batch hydrothermal [22–24] and sol–gel [25,26] methods. These methods can require multiple steps, are often energy intensive, can require special precursors (expensive and possibly atom inefficient), and such processes are often susceptible to batch-to-batch variations. In contrast, continuous synthesis methods can offer excellent control over reaction kinetics or particle parameters, use of relatively inexpensive precursors, greater product consistency and the potential for scale up [27–30].

This work describes the continuous hydrothermal flow synthesis (CHFS) of nano-sized layered titanate nanosheets, which were investigated as anode materials for lithium-ion batteries without any further processing. The nano-sheet material was evaluated by cyclic voltammetry in the potential range of 0.05–2.1 V *vs* Li/Li^+. The impact of charge/discharge rates on the charge storage mechanism was analysed and showed an expected shift towards more charge storage *via* surface effects at higher rates. Moreover, the materials showed excellent long term capacity retention during repeated cycling as high power anode materials.

2. Experimental

2.1. Materials

Titanium(IV) bis(ammonium lactato)dihydroxide solution (TiBALD, 50 wt.% in H_2O, Sigma Aldrich, Steinheim, Germany) and NaOH (Fisher Scientific, Loughborough, UK) were used as obtained as precursors for the synthesis under supercritical conditions.

2.2. Materials synthesis

The layered titanate nanoparticles were synthesised using a continuous hydrothermal flow synthesis (CHFS) reactor, incorporating a confined jet mixer (CJM, application no. GB1008721), the basic design of which is described elsewhere [31,32]. The laboratory scale CHFS process is similar to the pilot scale CHFS process, which has been the subject of previous publications [33,34] but on *ca.* 1/5 of the pilot scale [35]. A schematic diagram of the laboratory scale CHFS reactor used herein, is presented in Fig. 1 [32,34,36–38].

Three identical diaphragm pumps (Primeroyal K, Milton Roy, Pont-Saint-Pierre, France) were used to supply three independent feeds, which were pressurised to 24.1 MPa (Fig. 1). A 0.3 M aqueous solution of TiBALD (precursor 1) was supplied at a flow rate of 40 mL min^{-1} by pump 1. A second feed of 12 M NaOH (precursor 2) was supplied at a flow rate of 40 mL min^{-1} by pump 2. These two precursor feeds were premixed in flow at room temperature in a dead volume tee piece and then the combined mixture was then brought into contact with a flow of supercritical water at *ca.* 450 °C and 24.1 MPa (sc-water flow rate = 80 mL min^{-1}) in the CJM. The CJM was designed to eliminate blockages under these conditions and facilitated highly efficient mixing. The reaction residence time was calculated to be *ca.* 2.7 s at a reaction temperature of 335 °C. The newly formed particles were then cooled in process using a pipe-in-pipe heat exchanger, before exiting the process at ca. 40 °C (after first passing through a back-pressure regulator valve). At the end of the process, the nanoparticle laden slurry was collected and then cleaned by allowing the solids to sediment under gravity before washing briefly in DI water (10 MΩ). The wet solids were then freeze-dried (Virtis Genesis 35XL) at −60 °C for 24 h under a vacuum of <100 mTorr. The as-prepared freeze-dried powders were used (with no additional heat-treatments) for the slurry (containing a solvent, carbon, active and binder mixture) that was used to make the electrode.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns of the samples were obtained on a STOE diffractometer using Mo-Kα radiation ($\lambda = 0.707831$ Å), over the 2θ range 2–35° with a step size of 0.5° and step time of 30 s. The size and morphology of the particles were determined by transmission electron microscopy (TEM) using a Jeol JEM 2100 – fitted with a LaB_6 filament. The system was equipped with a Gatan Orius digital camera for digital image capture. The sample was prepared by ultrasonically dispersing the powder in >99.5% pure methanol (EMPLURA, Darmstadt, Germany) and dropping on to a copper film grid (300 mesh – Agar Scientific, Stansted, UK). Field emission scanning electron microscopy (FE-SEM) images were obtained with a JEOL JSM-6700F microscope operating at 5 kV accelerating voltage (sample diluted in methanol and then dropped on a pure silicon plate). Brunauer–Emmett–-Teller (BET) surface area measurements were carried out using N_2 in a micrometrics ASAP 2420 instrument. The sample was degassed at 150 °C (12 h) under vacuum, before measurements commenced. Raman spectra were collected with a Renishaw inVia™ Raman microscope (laser $\lambda = 514$ nm). The sample was diluted in ethanol and then dropped on a pure silicon plate. Thermogravimetric analysis (TGA) was performed using a Pyris 1 TGA instrument (Perkin Elmer) under nitrogen with a flow rate of 20 mL min^{-1} in the temperature range 25–700 °C with a heating rate of 10 °C min^{-1}.