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# Mesoporous TiO<sub>2</sub> nanocrystals produced by a fast hydrolytic process as high-rate long-lasting Li-ion battery anodes

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### Abstract

Mesoporous TiO<sub>2</sub> nanocrystals were prepared by a simple and fast hydrolytic process, in the presence of tetrabutylammonium bromide surfactant, and their ambient temperature electrochemical behaviour as high-rate Li-ion battery anodes was successfully demonstrated even after very long-term cycling (>1000 cycles). Samples were thoroughly characterized by X-ray diffraction, transmission electron microscopy, nitrogen physisorption analyses and electrochemical techniques. Using a novel synthesis approach, regular mesoporous TiO<sub>2</sub> anatase phase with a specific surface area of 258 m<sup>2</sup> g<sup>-1</sup> and a good degree of crystallinity was directly obtained without further treatments. The material was also calcined at different temperatures between 250 and 550 °C, to increase the degree of crystallization and assess the influence of the structural modifications on the electrochemical characteristics. Very good rate capability and excellent stability upon very prolonged cycling were achieved, thus indicating the prospects of the prepared materials for next-generation high-power lithium-based batteries.

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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 [2,3]. TiO<sub>2</sub> polymorphs, typically anatase, rutile and brookite, are characterized by a relatively high theoretical capacity (335 mA h g<sup>-1</sup>, considering the intercalation of 1 Li<sup>+</sup> per TiO<sub>2</sub> which is close to the 372 mA h g<sup>-1</sup> for graphite), negligible lattice changes during Li ion insertion/extraction (<4% for anatase) and a lithium ion insertion/deinsertion potential in the range of 1.5–2.0 V vs. Li<sup>+</sup>/Li. Hence, the material is inherently safer than graphite by avoiding Li electroplating and making the formation of a solid–electrolyte interface unlikely [4,5]. The main disadvantage arising from the high Li<sup>+</sup> insertion/deinsertion potential of TiO<sub>2</sub> is that it lowers the overall cell working potential with respect to graphite when coupled with the same cathode [6]. Another drawback, limiting the electrochemical performance of TiO<sub>2</sub> electrode materials,

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is the poor ionic and electronic conductivity of  $TiO_2$ . The reversible lithium ion insertion into and extraction from  $TiO_2$  [7–9] occur according to the following reaction:

$$x\mathrm{Li}^+ + \mathrm{TiO}_2 + x\mathrm{e}^- \leftrightarrow \mathrm{Li}_x\mathrm{TiO}_2$$
 (I)

where x can range between 0 and 1, depending on the  $TiO_2$ polymorph, particle size and morphology [10]. Generally, TiO<sub>2</sub> anatase can reversibly uptake 0.5 Li<sup>+</sup> per formula unit through a biphasic mechanism which comprises the Li-poor tetragonal Li<sub>0.05</sub>TiO<sub>2</sub> and the Li-rich orthorhombic Li<sub>0.5</sub>TiO<sub>2</sub> [8], leading to a theoretical capacity of  $\sim 167 \text{ mA h g}^{-1}$ . On the other hand, rutile and brookite are able to accommodate only small numbers of lithium ions [2,10–13]. Anatase is a typical insertion material: almost half of its available interstitial octahedral sites can be randomly occupied by  $Li^+$  ions [1], and thus its electrochemistry is largely particle-size-dependent [14]. Thus, its electrochemical properties (e.g., specific energy, storage capacity, high current discharge/charge ability and cycling stability) may be improved by nanostructuring the electrodes [15–17]. Indeed, those compounds that in the bulk form possess low Li diffusion coefficients usually exhibit low lithium ion storage capacities at high-current regimes [18].

In 2007, Jiang et al. [19] carefully described the different contribution of small TiO<sub>2</sub> particle size (implying short  $Li^+$ and electron transport lengths) and that of high specific surface area, which has been related to the high and fast Li storage at the surface. When cycling anatase electrodes at high current regimes, the shrinkage of the charge/discharge plateau can be delayed by decreasing the TiO<sub>2</sub> particle size, the Li storage at the surface being almost independent of the current rate and cycle number. Thereby, nanostructured electrodes can perform stable charge/discharge cycles, even at high current rates [18,20]. Accordingly, for large-scale production of safe energy storage devices, it is important to identify high-surface-area, inexpensive and conductive nanosized materials that can be integrated into batteries to improve their high rate performance at reduced cost [4].

Relying on these considerations, we propose a simple and fast synthetic route for the preparation of  $TiO_2$  nanocrystals having a mesoporous architecture by the hydrolysis of titanium(IV) isopropoxide in the presence of a surfactant. Such a method was inspired by the approach proposed by Mendez et al. [21] for producing pristine and functionalized titania nanosized crystallites as gold catalyst supports for CO oxidation and aerobic stilbene epoxidation and here proposed for the first time for the elaboration of stable and long-lasting Li-ion battery electrode active materials.

## 2. Experimental

### 2.1. Synthesis

The synthesis involves the use of titanium(IV) isopropoxide  $Ti(O-i-Pr)_4$  (purity 99.999%, Aldrich) as  $TiO_2$  precursor. The precursor was added dropwise and under continuous stirring, to a tetrabutylammonium bromide surfactant solution at the boiling point. Due to the high reactivity of  $Ti(O-i-Pr)_4$ , all the operations were performed under Ar atmosphere. Immediately after the hydrolysis, the suspension was kept at 100 °C for 3 h. Afterwards, the obtained white powder was collected by centrifugation and washed several times with a mixture of water and ethanol, to remove the excess of surfactant, then dried at ambient conditions.

From the same batch of synthesis, five aliquots were obtained. The as-prepared sample was labelled TiO<sub>2</sub>-NC and used without further treatments. The remaining four aliquots were then subjected to a 4 h calcination step under flowing air at four different temperatures (i.e., 250, 350, 450 and 550 °C), which were labelled as TiO<sub>2</sub>-250, TiO<sub>2</sub>-350, TiO<sub>2</sub>-450 and TiO<sub>2</sub>-550, respectively.

### 2.2. Structural-morphological characterization techniques

X-ray diffraction patterns were obtained using a Philips Xpert MPD powder diffractometer, equipped with Cu K $\alpha$ radiation (V = 40 kV, i = 30 mA) and a curved graphite secondary monochromator. The diffraction profiles were collected in the  $2\theta$  range between  $20^{\circ}$  and  $70^{\circ}$ , with an acquisition step of  $0.02^{\circ}$  and a time per step of 10 s.

Nitrogen adsorption-desorption isotherms at 77 K were collected on an ASAP 2020 Micromeritics instrument. Prior to adsorption,  $\sim 100$  mg of solid were placed in the cell and evacuated at 300 °C for 3 h under high vacuum. Specific surface areas (SSAs) were determined using the Brunauer-Emmet-Teller (BET) method, whereas the pore diameter distribution was evaluated by the Barrett-Joyner-Halenda (BJH) method, with the corrected form of the Kelvin equation, from the desorption branch of the isotherms.

High-resolution transmission electron microscopy (HRTEM) investigations were carried out using a JEOL 2010 microscope with an accelerating voltage of 200 kV.

# 2.3. Electrodes preparation, cell assembly and electrochemical characterization

Electrodes (geometrical area 2.54 cm<sup>2</sup>,  $\sim$ 7 mg of active material weight) were prepared in the form of films over a copper foil (Goodfellow, thickness 0.0125 mm) current collector. A *N*-methyl-2-pyrrolidone (NMP, Aldrich) slurry of the TiO<sub>2</sub> active material mixed with acetylene black (Shawinigan Black AB50, Chevron Corp., USA) as electronic conducting additive and polyvinylidenefluoride as binder (Solvay Solef-6020), in the weight ratio of 70:20:10, was deposited over the current collector using a standard "doctor blade" technique.

Both two- and three-electrode electrochemical cells were employed to evaluate the electrochemical performance of the different samples. In a typical test, the cell was assembled as follows: a working electrode having the above described composition, a 1.0 M lithium hexafluorophosphate (LiPF<sub>6</sub>) in a 1:1 w/w mixture of ethylene carbonate and diethyl carbonate liquid electrolyte solution (Solvionic, France, battery grade) soaked on a Whatman<sup>®</sup> GF/A separator and a lithium foil (high-purity lithium foils, Chemetall Foote Corporation) as counter-electrode. The lithium test cells (model ECC-Std and ECC-Ref for galvanostatic cycling and cyclic voltammetry, respectively) were purchased from EL-Cell, Germany (http://el-cell.com/products/test-cells). Lithium metal was used both as the counter-electrode (foil) and as the reference electrode (rod).

Galvanostatic discharge/charge cycling and cyclic voltammetry were obtained at ambient temperature using an Arbin Instrument Battery Testing System model BT-2000. During cyclic voltammetry, the electrode potential was reversibly scanned between 1.0 and 3.0 V vs. Li<sup>+</sup>/Li at 0.100 mV s<sup>-1</sup>. The scan started from the cell open circuit potential towards the reduction branch of the potential scan. The galvanostatic discharge/charge cycles were carried out between cutoff potentials of 1.0 and 3.0 V vs. Li<sup>+</sup>/Li, at different current regimes ranging from C/10 to 10 C rates. In the tests, discharge refers to lithium insertion and charge refers to lithium extraction into/from the active material structure. All measurements were performed at ambient temperature conditions.

### 3. Results and discussion

### 3.1. Structural and morphological results

The X-ray powder diffraction (XRPD) analysis of the prepared samples is depicted in Fig. 1. It shows that the diffraction intensities of crystalline TiO<sub>2</sub> for all the samples increase with the calcination temperature [5]. Although the TiO<sub>2</sub>-NC sample pattern presented weak and broad peaks, indicating a low degree of crystallinity of the uncalcined TiO<sub>2</sub> sample, the (101), (004), (200), (211), (220) and (204) diffractions typical of anatase  $TiO_2$  (JCPDS Card No. 04-0477, space group: I41/amd) could be detected. This indicates that crystalline TiO<sub>2</sub> nanoparticles already existed after the hydrolysis process [20] without need of any further heat treatment. For all the nano-TiO<sub>2</sub> synthesized powders, trace amounts of brookite phase (JCPDS Card No. 01-076-1936, space group Pbca) coexisted with the anatase phase as indicated in Fig. 1 (labelled by asterisks). The possible presence of small amounts of brookite phase within the nano-TiO2 anatase was confirmed by comparison with the literature data [11,22]. The sharpening of the XRPD peaks for the calcined powder with heat treatment indicated a growth of crystallite size upon calcination [23], as highlighted by the shape of the main intense (101) peak in the pattern of the different samples (Fig. 2). In fact, the full width at half maximum (FWHM) of each of the peaks became smaller with the increase in calcination temperature (Fig. 1), which is mainly due to an increase in crystallinity and crystallite size [24]. The crystallite size was calculated by evaluating the FWHM to the (101) peak applying the Debye-Scherrer



Fig. 1. XRPD  $(2\theta = 20-70^{\circ})$  of the TiO<sub>2</sub> samples calcined at different temperatures: TiO<sub>2</sub>-NC (red line), TiO<sub>2</sub>-250 (grey line), TiO<sub>2</sub>-350 (green line), TiO<sub>2</sub>-450 (orange line), TiO<sub>2</sub>-550 (blue line), along with the corresponding TiO<sub>2</sub> anatase and brookite reference patterns. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 2. XRPD patterns in the range of  $2\theta$  between  $23^{\circ}$  and  $28^{\circ}$  of the TiO<sub>2</sub> samples calcined at different temperatures: TiO<sub>2</sub>-NC (red line), TiO<sub>2</sub>-250 (grey line), TiO<sub>2</sub>-350 (green line), TiO<sub>2</sub>-450 (orange line), TiO<sub>2</sub>-550 (blue line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

equation. Substantial differences among samples TiO<sub>2</sub>-NC, TiO<sub>2</sub>-250 and TiO<sub>2</sub>-350 were not detectable and, as the scattering domains were very small, the average particle size was  $\sim 6$  nm for the three samples. Sample TiO<sub>2</sub>-450 showed a slight increase of crystallite size to  $\sim 8$  nm, whereas a more pronounced difference was observed for

sample TiO<sub>2</sub>-550 with a crystallite size of  $\sim$ 13 nm. Therefore, calcination at 550 °C of the pristine product led to a marked increase in the grain size and in the crystalline degree, but the anatase crystal phase was kept unchanged.

Samples TiO<sub>2</sub>-NC and TiO<sub>2</sub>-550 have given further insight into the phase structure and electrochemical characterization as they respectively possessed the lowest and the highest crystallite size among the various samples. BET measurements were carried out to assess the changes in the SSA after calcination. The not-calcined TiO<sub>2</sub>-NC sample exhibited a SSA of 258 m<sup>2</sup> g<sup>-1</sup>, which corresponded to the theoretical external surface of 6 nm TiO<sub>2</sub> crystallites (assuming spheres with a density of  $3.9 \text{ g ml}^{-1}$ ) [21], while the calcined TiO<sub>2</sub>-550 showed a value of  $122 \text{ m}^2 \text{ g}^{-1}$ . Thus, the SSA was  $\sim$ 55% lower for the calcined sample with respect to the not-calcined counterpart. This was consistent with the increase of the grain size and particle growth at high temperature observed by XRPD and confirmed by literature data [23,24]. The heat treatment, indeed, is reasonably an effective way to improve the crystallinity of the TiO<sub>2</sub> anatase, but it inevitably causes a decrease in surface area due to the coalescence of the inorganic framework [25]. However, it is worth noting that the BET values of sample TiO<sub>2</sub>-550 obtained by our fast hydrolytic route are surprisingly high if we consider, for instance, the values of  $60.3 \text{ m}^2 \text{ g}^{-1}$  for TiO<sub>2</sub> prepared by hydrothermal synthesis and calcined at 500 °C, as reported by Oh et al. [24] or 29.49 m<sup>2</sup> g<sup>-1</sup> for TiO<sub>2</sub> nanoparticles annealed at 500 °C, as reported by Rai et al. [23].

Additionally, Fig. 3 depicts the results from nitrogen sorption measurements, where the plot shows a type-IV isotherm with a clear H1-type hysteresis loop. For both the samples, the presence of a sharp decrease in the relative pressure range of 0.4-0.7 is related to a well-developed mesoporosity with a non-ordered pore distribution. As previously stated, the crystal size and the pore size increased as a result of the calcination treatment, while the BET surface area decreased as well as the pore volume; again such a difference could be explained by considering the coalescence among the grains leading to the decrease of voids among particles. The average pore diameter, calculated using the BJH method from the desorption branches of the isotherm, was centred at 8.0 nm for TiO<sub>2</sub>-NC; after calcination at 550 °C it increased to 10.0 nm (TiO<sub>2</sub>-550). Furthermore, the total pore volume decreased from  $0.577 \text{ cm}^3 \text{ g}^{-1}$  (TiO<sub>2</sub>-NC) to  $0.364 \text{ cm}^3 \text{ g}^{-1}$  (TiO<sub>2</sub>-550), indicating that the heat treatment resulted in a small collapse of the pore system. Thus, the mesoporous structure of the two samples could be ascribed to the inter-particle space caused by the random stacking of TiO<sub>2</sub> nanoparticles [26] and this is reflected in the HRTEM pictures reported in Figs. 4 and 5. TEM images revealed that the samples possessed a nanoparticle-agglomerated mesoporous structure where the nanosized grains, homogeneous in size and shape, possessed an almost spherical morphology. Differences in crystallinity were clearly visible by analyzing the micrographs at higher magnification (Figs. 4b and 5b) as



Fig. 3. Nitrogen adsorption/desorption isotherms at 77 K of  $TiO_2$ -NC (red line) and  $TiO_2$ -550 (blue line) samples. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

already discussed during XRPD analysis. Sample TiO<sub>2</sub>-550 still possessed the particulate morphology; however, the product aggregated severely if compared to TiO<sub>2</sub>-NC, due to the coalescence of nanoparticles that were subjected to faster crystallization [11,23]. Characteristic lattice fringes of anatase TiO<sub>2</sub> were also clearly visible (Fig. 5b). Moreover, calcination at 550 °C of the as-prepared powder not only increased the particle size, but also seemed to promote the formation of a harder porous network through the aggregation of the nanocrystals. Such architecture might be beneficial in terms of improving the mechanical integrity of the material and by enhancing the electronic conduction among the particles [20].

### 3.2. Electrochemical results

A series of electrochemical measurements were carried out in order to assess the storage capability and the cycling performance of the two TiO<sub>2</sub> samples in laboratory-scale lithium cells. Fig. 6a and b display representative cyclic voltammograms (CVs) of TiO2-NC and TiO2-550 samples at the scan rate of  $0.100 \text{ mV s}^{-1}$  recorded between 1.0 and 3.0 V vs. Li<sup>+</sup>/Li. CV profiles are very similar and consistent with those reported in the literature for nanocrystallite anatase electrodes [10,24]. Referring to plot (a), two welldefined peaks can be observed at  $\sim 1.75$  V (cathodic scan) and 1.98 V (anodic scan) vs. Li<sup>+</sup>/Li. The cathodic peak is traditionally associated to the two-phase transition of the crystalline structure from tetragonal anatase to orthorhombic  $Li_{0.5}TiO_2$  (Ti<sup>4+</sup> to Ti<sup>3+</sup>) [27,28]. The anodic peak, centred at ~1.98 V vs. Li<sup>+</sup>/Li, is related to the Ti<sup>3+</sup> oxidation to Ti<sup>4+</sup> upon lithium extraction and, with the peak current densities being almost equal for both the cathodic and anodic processes, the overall Coulombic efficiency is high. Here, Coulombic efficiency refers to the per cent ratio between the specific capacity values during discharge (Li<sup>+</sup> ions insertion) and charge (Li<sup>+</sup> ions de-insertion). A



Fig. 4. HRTEM micrographs of sample TiO<sub>2</sub>-NC at different magnifications.



Fig. 5. HRTEM micrographs of sample TiO<sub>2</sub>-550 at different magnifications.

particular feature of these samples is the presence of a small peak in the cathodic branch (at  $\sim 1.50$  V vs. Li<sup>+</sup>/Li for both samples), which had a correspondence in the following anodic scan, where a broad shoulder is visible. Typically, in the presence of brookite phase, the presence of which in our samples was detected by XRPD analysis (see Fig. 1), such additional peaks are associated with different site occupations and attributed to the formation of imperfections in the TiO<sub>2</sub> lattice, which facilitate the lithium ion transport through surface defects [29]. As reported by Lee et al. [29], the presence of brookite does not affect the cycling behaviour as it can reversibly intercalate/deintercale lithium ions. Remarkable changes in the CV profiles during cycling were not observed and the shape of the CV profiles remained stable after the initial cycle, thus the Ti redox reaction associated with the lithium ions insertion/extraction can be considered a stable process and it occurs reversibly both in anatase and in brookite.

From a comparison between the two CV profiles, the peak separation decreases a little for  $TiO_2$ -NC (22 mV) compared to the  $TiO_2$ -550 (28 mV) and this indicates that the smaller particles ( $TiO_2$ -NC) are kinetically more favourable than the larger ones, and that less overpotential is required for the anatase-to-lithium titanate phase transformation process [20]. A similar trend in peak potential

separation was already reported by Subramanian et al. [11] for TiO<sub>2</sub> with different crystallite size, since the overpotential is generally lower for materials having higher surface area (in our case,  $258 \text{ m}^2 \text{ g}^{-1}$  for TiO<sub>2</sub>-NC with respect to  $122 \text{ m}^2 \text{ g}^{-1}$  for TiO<sub>2</sub>-550) and greater capacitive currents are generally associated with the smaller particles compared to the larger ones. Wang et al. [20] ascribed 55% of capacitive effects to the total lithium ion storage for particle sizes under 10 nm, leading to much faster charge/discharge kinetics than occurs with intercalation. Such an issue was less noticeable for TiO<sub>2</sub>-550, in which the larger particle size and the higher degree of crystallinity [24] make the material less sensitive to such effects.

The electrochemical behaviour in terms of specific capacity and rate capability upon very prolonged discharge/charge galvanostatic cycling was tested at different current regimes from C/10 to 10 C. The corresponding results are shown in Figs. 7 and 8. Even if both samples showed excellent behaviour in terms rate capability and differences between the sample were almost negligible, TiO<sub>2</sub>-550 resulted in slightly better overall performance in terms of specific capacity, which resulted in a slight of ~10% at each of the tested current regimes. The delivered specific capacity values after 10 cycles at low C/10 rate were ~158 mA h g<sup>-1</sup> for sample TiO<sub>2</sub>-NC and 163 mA h g<sup>-1</sup> for



Fig. 6. CV analysis of the samples: (a) TiO<sub>2</sub>-NC and (b) TiO<sub>2</sub>-550. Scan rate =  $0.100 \text{ mV s}^{-1}$  and voltage range =  $1.0-3.0 \text{ V vs. Li}^+/\text{Li}$ .

sample TiO<sub>2</sub>-550. Upon prolonged cycling, the Coulombic efficiency of sample TiO<sub>2</sub>-550 was always a bit higher than that of TiO<sub>2</sub>-NC; this might be related to the higher crystallinity of the material subjected to calcination [24]. When the samples were subjected to an increase in the current regime, the reversible capacity decreased to  $\sim$ 96 mA h g<sup>-1</sup> (TiO<sub>2</sub>-NC) and 110 mA h  $g^{-1}$  (TiO<sub>2</sub>-550) when cycled at 1 C rate. Nevertheless, at ambient temperature, both samples demonstrated an outstandingly long-term cycling stability: in fact, a reversible capacity of 89 mA h  $g^{-1}$  was retained after 1000 charge-discharge cycles for sample TiO<sub>2</sub>-NC and  $\sim$ 98 mA h g<sup>-1</sup> for sample TiO<sub>2</sub>-550 in the same experimental conditions at the 1 C rate. This means that both samples demonstrated a very good retention of the initial reversible capacity (>85%) at the same current regime. These excellent results were even more appreciable when considering the specific capacity values of  $65 \text{ mA h g}^{-1}$  (TiO<sub>2</sub>-NC) and 70 mA h g $^{-1}$  (TiO<sub>2</sub>-550) delivered after 100 discharge/charge cycles at high current rate (10 C). It is noteworthy that the first discharge capacity of  $\sim$ 240 mA h g<sup>-1</sup> can be reached, at C/10, which corresponds to a lithium insertion coefficient of  $\sim 0.7$ , which is higher than the theoretical value of 0.5. The irreversible capacity loss observed is generally related to the inability



Fig. 7. Specific discharge/charge capacities and Coulombic efficiency upon cycling of  $TiO_2$ -NC sample. Here, Coulombic efficiency refers to the per cent ratio between the specific capacity values during discharge (Li<sup>+</sup> ions insertion) and charge (Li<sup>+</sup> ions de-insertion).

to extract from the material all the inserted lithium in the first cycle, during the subsequent cycles [23].

The load curves (potential vs. time profiles) of the two different anatase samples collected at various C rates are reported in Fig. 9a and b. Discharge/charge profiles are consistent with those reported in the literature [19,23,30] and a strong dependence of the Li storage characteristics to the crystallites size was clearly observed. At C/10, almost 0.5 Li reacted with the TiO<sub>2</sub>-550, corresponding to a specific capacity of 169 mA h g<sup>-1</sup> and 0.46 Li reacted with the TiO<sub>2</sub>-NC for a delivered capacity of 153 mA h  $g^{-1}$ . A careful analysis of the shape of the discharge profiles suggested some differences in the electrochemical behaviour of the materials. The first discharge region is usually characterized by a steep potential decrease, which corresponds to a small fraction of Li uptake by the tetragonal anatase through a solid solution mechanism; such a process is considered irreversible during the first discharge/charge and it is accompanied by very small capacities during the subsequent cycles [19,30,31]. Thereafter, a potential plateau at  $\sim$ 1.75 V vs. Li<sup>+</sup>/Li is indicative of the biphasic intercalation process involving the tetragonal TiO<sub>2</sub> and orthorhombic  $Li_{0.5}TiO_{2}$ . Both the anatase and the lithium titanate phases coexist up to a certain particle diameter; below that



Fig. 8. Specific discharge/charge capacities and Coulombic efficiency upon cycling of  $TiO_2$ -550 sample. Here, Coulombic efficiency refers to the per cent ratio between the specific capacity values during discharge (Li<sup>+</sup> ions insertion) and charge (Li<sup>+</sup> ions de-insertion).

limit, less lithium insertion is required to convert the particle to the lithium titanate phase [20]. A consequence is the shortening of the plateau region as the particle size decreases.

In our present case, the shorter plateau at 1.78 V vs. Li<sup>+</sup>/Li observed for the TiO<sub>2</sub>-NC, compared to that of TiO<sub>2</sub>-550, suggests that the number of available interstitial octahedral sites, necessary for Li insertion, decreased with the particle size although the diffusion of lithium occurred on a shortest path. According to Qiao et al. [30], since the biphasic intercalation process is generally associated to changes in the lattice volume, materials characterized by a well-developed plateau should be more sensitive to lattice strains, resulting in a faster capacity fading during cycling. In our case, no appreciable changes in the characteristic shapes (only a slight overpotential) of the potential profiles, even after 300 cycles at very high 10 C rate, could be noticed for both the samples, suggesting that no observable degradation of the materials occurs during the lithium insertion/extraction processes after being confirmed by the outstanding very long-term cycling stability.

A comparison between the potential profiles for  $TiO_2$ -NC and  $TiO_2$ -550 below the flat-band (i.e., in the potential window from 1.78 V to 1.0 V vs.  $Li^+/Li$  in Fig. 9a and b)



Fig. 9. Potential vs. time profiles at different current rate extracted from the galvanostatic cycling test of (a)  $TiO_2$ -NC and (b)  $TiO_2$ -550.

showed that the capacity of this third sloped region increased correspondingly to the specific surface area of the anatase material. Usually, the extension of this region is related to a further lithium insertion into Li<sub>0.5</sub>TiO<sub>2</sub> and material having a prolonged sloped region can accommodate more lithium ions, thus releasing higher reversible capacity [30]. The delivered discharge capacity at C/10 within this potential region was more than two-thirds for TiO<sub>2</sub>-NC, compared to about half of the total discharge capacity for TiO<sub>2</sub>-550 sample. Jiang et al. [19] observed a quite similar behaviour when cycling commercially available anatase nanopowders and they concluded that this stage of lithium insertion is principally dominated by surface effects, as the capacity of the sloped region is strongly dependent on the specific surface area of the anodic material.

Comparing the results of our mesoporous anatase nanocrystals with those obtained previously for similar  $TiO_2$ nanoparticles [11,23,24,30,32,33], excellent rate capability and cycling stability were demonstrated for very prolonged cycling, especially if one considers sample  $TiO_2$ -NC, which is directly obtained after a fast hydrolytic process, without the need of any further time- and energy-consuming heat treatment. The presence of mesopores is thought to be also important for high rate performances and favourable for electrolyte ions transport [33]. Moreover, the present work suggests the reliability of our hydrolytic process when compared to other solution-based methods that generally require multi-step procedures and/or very high temperature treatments to obtain the desired crystalline phases.

### 4. Conclusions

In this study we presented a simple method to directly synthesize mesoporous  $TiO_2$  anatase nanocrystalline powders, evidencing highly interesting electrochemical performances, even without the need for further heat treatment. Both calcined and not-calcined samples showed good specific capacity values along with rate capability and, particularly, excellent long-term cycling stability, which were related to the uniform and homogeneous structure of the nanocrystalline TiO<sub>2</sub> powders.

The obtained values were due to two different prevalent mechanisms. Actually, sample TiO<sub>2</sub>-NC showed a higher SSA (more than twice that of TiO<sub>2</sub>-550) and, correspondingly, in its profile the portion due to the surface contribution was indeed the prevalent fraction. On the other hand, for sample TiO<sub>2</sub>-550, which showed enhanced crystallinity, the contribution of Li<sup>+</sup> ions insertion into bulk anatase crystals became important, as evidenced by the presence of a flatter plateau.

Particularly noteworthy, considering a possible practical application, was the as-prepared  $TiO_2$ -NC sample. Actually, beyond its general good performances, only 10% lower than the calcined one, its synthesis procedure is quick and easy to perform, especially because a calcination step is not necessary. This fact is significant, bearing in mind the increasing requirement for low-cost and environmentally friendly materials. Thus, we can conclude that  $TiO_2$ -NC material is particularly attractive for large-scale production where stable electrochemical performance must be associated with a simple, fast and low-cost material production.

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