Ordered mesoporous oxide for thin film microbatteries with enhanced lithium storage

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Abstract

A 3D mesoporous TiO₂ material with well-developed mesostructure is prepared in the form of a binderless thin (100 nm) film and studied as potential candidate for the negative electrode in lithium micro-batteries. By appropriate thermal treatments, the selected crystal structure (anatase, rutile, or amorphous), and micro-/mesostructure of the materials was obtained. An extended plateau with at about 0.75 V was found for an X-ray amorphous TiO₂ sample (400 °C) which can be tentatively assigned to the irreversible formation of cubic-Li₂Ti₂O₄. The effects of voltage window and prelithiation treatment improved first cycle reversibility up to 86 % and capacity retention of 90 % over 100 cycles. This study highlights the flexibility of the potential window to which the electrode can operate. Maximum capacity values over 100 cycles of 470 $\mu\text{A h cm}^{-2} \mu\text{m}^{-1}$ and 177 $\mu\text{A h cm}^{-2} \mu\text{m}^{-1}$ are obtained for voltage ranges of 0.1 – 2.6 V and 1.0 – 2.6 V, respectively. The observed values are between 6 and 2 times higher than those obtained for films with 600 nm (80 $\mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$) and 900 nm (92 $\mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$) lengths. This indicates that 100 nm thin TiO₂ films with high accessibility show finite-length type diffusion which is interesting for this particular application.

Keywords: Ordered mesoporous TiO₂, binderless electrodes, Li-ion microbatteries, improved lithium storage

1. Introduction

The excellent performance of rechargeable lithium-ion batteries (LIBs) has enabled the wireless revolution of electronic devices such as computers, digital cameras or cell phones that has transformed global communications. Nowadays the performance of LIBs is dominated by the chemistry design of electrode materials [1,2]. For high-power applications of LIBs, it is recommendable to find anode materials alternative to graphite due to its low capacity at high rates and low reaction potential (close to 0.1 V vs. Li^+/Li^0) [3,4]. Therefore, the scientific community is still exploring potential candidates. Upon reaching this goal, safety in batteries could be achieved. For instance, metal oxides have represented an interesting class of anode materials due to their high capacities [4]. Among metal oxide materials, TiO_2 has been widely considered because of several aspects such as intercalation-based reaction with lithium, high stability, nontoxicity and abundance among others. From a structural point of view titanium dioxide displays a variety of crystalline polymorphs including anatase, rutile, $\text{TiO}_2\text{-B}$, brookite, ramsdellite (R), hollandite (H), columbite and baddeleyite. Among them, only anatase, rutile brookite and $\text{TiO}_2\text{-B}$ have been tested for LIB applications [5-8]. Also, TiO_2 presenting X-ray amorphous phase have been readily investigated exhibiting an excellent capacity and long cycling life, but still suffers from high irreversibility in the first cycle and needs of a wide voltage window to deliver reasonable capacity (170 – 200 mA h g^{-1}).

The main drawback of the TiO_2 polymorphs is the poor Li ion diffusion and accompanying electrons in its bulk form which restricts the full material utilization electrochemically [9-11]. To improve the intrinsic (charge/ion) transport properties, TiO_2 polymorphs must be prepared in nanostructure that could enhance the intercalation properties. Numerous nanostructured TiO_2 materials, such as nanotubes, nanofibers,

1 nanowires, and nanoparticles, were designed to improve its electrochemical
2 performance for LIBs [12-16]. Irrespective of their poor electrical conductivity, it has
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4 been demonstrated that a layer of self-organized TiO₂ nanotubes (ntTiO₂) is useful for
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6 alternative Li-ion batteries without conducting binders [6,7]. Indeed, for microelectronic
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8 industry it is desirable the use of thin film materials without additives since could
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10 reduce about a 20% of their size and weight. For instance ntTiO₂ layers of 900 and 600
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12 nm of nanotube length growth directly from Ti current collectors exhibited volumetric
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14 capacity of about 80 and 90 $\mu\text{A h cm}^{-2} \mu\text{m}^{-1}$, respectively [6,7].
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19 Brinker and co-workers [17] developed a simple and straightforward approach to
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21 fabricate thin films based on phenomenon known as Evaporation-Induced Self-
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23 Assembly. By a careful control of the synthesis conditions, as well as of the
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25 composition of the precursor solution, the relative humidity during the solvent
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27 evaporation stage or the thermal treatment to which the resulting thin film is submitted
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29 to, the composition of the nanostructured coatings and their porous structure may be
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31 controlled [18]. From this perspective, the simplest approach would be to use a well-
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33 established methodology such as dip-coating to transfer a TiO₂ film with a thickness
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35 under 100 nm to a substrate which could be employed as current collector [19].
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41 The objective of our work is to prepare homogeneous thin film 3D-
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43 mesostructures of TiO₂ with thickness of 100 nm on Ti current collectors.
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45 Experimental results in Li cells demonstrated an improved performance of 100 nm thick
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47 film in terms of high capacity, long cycle life, and high rate capability in microbatteries.
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49 The poor conductive properties of titania commonly requires de use of carbon additives
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51 to facilitate electrical contact between nanoparticles, as well as binders to achieve the
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53 necessary mechanical stability of the electrodes. These additives decrease the overall
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55 electrode capacity and impose rigidity which impedes potential applications where
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flexible electrodes are required, such as the origami battery concept [20]. The electrode design developed in this work facilitates efficient electron transport while eliminating the need for binders and conductive carbon additives without jeopardizing their stability on long-term cycling. Thus, these materials are presented as interesting candidate as anode materials for Li-ion microbatteries (LIMBs).

2. Experimental

2.1. Materials and reagents: Titanium plates (1x1 cm) with a purity of 99.6+% were purchased from Goodfellow. Triblock copolymers pluronic P123 (EO20PO70EO20, M=5800) and F127 (EO106PO70EO106, M=12600) were kindly donated by BASF chemical company and used as templates. Titanium tetraisopropoxide (TTIP) and titanium tetrachloride (TiCl₄) were purchased from Sigma Aldrich and used as Titanium sources. All reagents were used as received with no further purification.

2.2. Thin film preparation: Mesoporous TiO₂ thin films were grown on flat Ti plates by two different routes found in the literature which give rise to 3D hexagonal (*P6₃/mmc* symmetry) [21] and cubic (*Im-3m* symmetry) [22] thin films, respectively. All Ti samples were wiped clean with a cloth impregnated with absolute EtOH to remove any dust or particles from the surface of the plates.

In synthetic protocol (1), 1.05 g of Pluronic P123 were added to 16.21 g of absolute ethanol. The solution was stirred until completely clear, and then 4.03 g of concentrated (37%) HCl were added dropwise. To the resulting mixture, 5.70 g of TTIP were added dropwise, giving the final solution the following molar composition: 1 TTIP:0.01 P123:17.6 EtOH:1.9 HCl:7.2 H₂O.

1 In synthetic protocol (2), 0.51 g of Pluronic F127 were dissolved in 14.71 g of
2 absolute ethanol by gentle heating and under strong stirring. To this clear homogenous
3 solution 880 μL of TiCl_4 were added very slowly and under vigorous stirring to give a
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5 solution with the following molar composition: 1 TiCl_4 :40 EtOH: 0.005F127.
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9 Titania films were produced by dip-coating at a withdrawal speed of $1 \text{ mm}\cdot\text{s}^{-1}$.
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11 The Titanium substrates were rinsed with absolute EtOH prior to deposition. The
12 relative humidity (RH) during dip-coating was set at 50%. After deposition, films were
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14 aged at RH 50% for 24 h. Calcination of the films was performed either in a vacuum
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16 furnace at 300°C under high vacuum conditions for 1 hour or in a muffle furnace at
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18 either 400 , 550 , or 700°C for 1 hour. In all experiments, the heating rate was
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20 $1^\circ\text{C}/\text{minute}$.
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29 **2.3. Characterization:** X-ray diffraction (XRD) patterns were recorded at room
30 temperature using a Siemens D5000 diffractometer with $\text{Cu K}\alpha$ radiation ($1.54056 \text{ \AA}$).
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32 The synthesized thin films were characterized by transmission electron microscopy
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34 (TEM) using a JEOL JEM-2010 high-tilt instrument operating at 200 kV with a
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36 structural spatial resolution of 0.5 nm . The samples were scratched off from the Ti
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38 surface and recovered with a droplet of ethanol. Then the suspensions were dropped
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40 gently on a holey amorphous carbon film on a Cu sample holder. The composition of
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42 the nanoparticles was measured by EDS coupled to the TEM equipment (OXFORD
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44 instruments model INCA Energy TEM100). The thin films were also characterized by
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46 Scanning Electron Microscopy (SEM) in a HITACHI S-3000N microscope and the
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48 thickness of the thin film prepared was studied.
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2.4. Electrochemical tests: The electrochemical performance of the mesoporous TiO₂ layers is studied by experiments carried out in Li/LiPF₆ (EC:DEC)/TiO₂ cells. The electrolyte supplied by Merck was embedded in a Whatman glass microfiber acting as a separator. For these experiments no additives such as poly(vinyl difluoride), that acts as binder agent, or carbon black (conductive agent) were used. The cells are assembled in a glovebox filled with purified argon in which moisture content and oxygen level were less than 2 ppm. Lithium cells were galvanostatically cycled using an Arbin potentiostat/galvanostat multichannel system. For the discharge/charge reaction a constant current density of 5 $\mu\text{A cm}^{-2}$ was applied to the assembled cells using two different voltage ranges: 0.1-2.6 V and 1.0-2.6 V. The prelithiation treatment was performed by pressing a lithium disk on the titania film at 0.22 N cm⁻² for 10 h under an Ar atmosphere.

3. Results and discussions

Fig. 1 shows the X-ray diffraction pattern of the mesoporous TiO₂ layers prepared on Ti plates at different temperatures using synthetic protocol (1) as a representative example of the samples analyzed in this study. A common characteristic of these XRD patterns is that they exhibit diffraction peaks ascribable to hexagonal Ti (PDF # 05-0682, S.G.: *P6₃/mmc*), the plate on which TiO₂ was growth. An X-ray amorphous character is evidenced for samples heated at 300°C under vacuum since no peaks corresponding to crystalline TiO₂ were observed. It is worth noting that our Ti plates showed the preferred growth orientation on (002), as shown by a comparison of the 002/101 reflection intensity ratio with the database. When the films were thermally annealed at 400 °C, no reflections ascribable to anatase TiO₂ were observed (Fig. 1).

1 This result is in apparent contradiction with the conversion of mesoporous TiO₂
2 powders to the anatase structure at 400°C reported by Kubiak et al [23]. This particular
3 difference is most probably a consequence of the low amount of active material
4 deposited on the Ti current collector as compared with powder samples together with a
5 low crystallite size in the films obtained at 400 °C. The presence of anatase will be
6 confirmed below by using electrochemical characterizations in the Li test cell.
7 However, after annealing at 550 °C broad an low intense reflections are observed at
8 about 25.3° and 47.9°, which correspond to the *101* and *200* reflections of the anatase
9 phase (JCPDS file #21-1272), respectively. In addition, the films obtained at 550°C also
10 showed low intensity reflections ascribable to rutile rutile (JCPDS file #21-1276). A
11 clearer view of the diffraction peaks is found for sample at 700 °C where new peaks
12 with high intensity emerged, ascribable to the presence of high crystalline anatase and
13 rutile phases, respectively (Fig. 1).

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34 The development of the mesostructure of the thin films was verified by TEM.
35 Fig. 2 shows the images of the as-synthesized thin films and those obtained after
36 calcination in vacuum. The images clearly show that the prepared thin films showed a
37 high quality mesostructure development with pore sizes between 4 – 5 nanometers.
38 Calcination of the samples did not alter the porous structure, which confirmed the
39 stability of the grown TiO₂ thin film resulting from the fine control of the synthesis and
40 ageing conditions. Electron microscopy was also used in order to determine the
41 thickness of the deposited thin film, which was estimated to be 100 nm.

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56 As the electrochemical storage based on lithium-ion intercalation represents one
57 of the most technologically advanced forms of energy storage, it is mandatory to

optimize the sample preparation and cycling conditions (e.g. voltage windows). The high value of the energy density and the versatility of the product in terms of fast charge/discharge and good capacity retention are the most studied parameters as well as the most important from a practical point of view. Briefly the Li insertion/deinsertion into the TiO₂ can be written as follows:

Theoretically, the insertion of 0.5 Li into the crystalline anatase phase gives a capacity value of 168 mA h g⁻¹ [24], and for 1.0 Li per Ti it reaches 336 mA h g⁻¹ or 1,297 mA h cm⁻³ (δ = 3.86 g cm⁻³). The electrochemical insertion of lithium ions takes place through a two-phase equilibrium of a Li-poor (tetragonal) and a Li-rich (orthorhombic) phase [25]. The orthorhombic phase formation is due to the accommodation of donated charge (Li donates an electron to the lattice) in localized Ti-d orbitals. Titanium ions in the anatase structure are arranged in a tetragonal configuration with [TiO₆] octahedral units. The distortion of the [TiO₆] octahedral unit is greater in the anatase than in the rutile phase. For Li-ion storage, the anatase TiO₂ phase is favorable because Li-ions readily penetrate into the structure and exhibit thermodynamic stability [26,27].

Figures 3 – 7 show the electrochemical properties for binderless 3D mesoporous TiO₂ thin film electrodes in the voltage range of 0.1 – 2.6 V and 1.0 – 2.6 V vs Li⁺/Li⁰ for synthesis protocol (1). The results for synthesis protocol (2) showed a poorer performance (not shown). This difference can be ascribed to the cubic (*Im-3m* symmetry) of the later thin films. The higher number of neighbor pores in *P6₃mmc* hexagonal packing may account for a better connectivity and lithium diffusivity. Another possible explanation would be that the two samples show different TiO₂

crystallite size, which in turn would affect the performance of the resulting electrode although this difference was not observable by X-ray diffraction or TEM. Figures 3 – 7 include the voltage profiles during the first 5 cycles, cycling performance and rate capabilities. The areal capacity is normally used to quantify the capacity for Li-ion microbatteries, and the volumetric capacity can also be deduced by taking into consideration the thickness of the film. To have comparative results with the literature, the current density used in this work is $5 \mu\text{A cm}^{-2}$ which is the same as those used for others TiO_2 thin film with 600 and 900 nm of thickness in previous reports [6,7]. All the samples thermally annealed at 400, 550 and 700 °C exhibit a discharge voltage plateau at 1.76 V and a charge voltage plateau at 1.92 V, which correspond to the intercalation/de-intercalation of Li ions from the interstitial octahedral sites of anatase TiO_2 [6,7,28]. However, a different reaction mechanism for the sample activated at 300 °C under vacuum was observed, which is typical of amorphous TiO_2 electrodes with a continuous decay of the potential from 3 to 0.1 V.

The amount of inserted Li^+ in the TiO_2 is dependent on whether the crystal structure is anatase, rutile or amorphous, as well as on the microstructure [3-6]. For the TiO_2 treated at 400 °C the total capacity in the first discharge was $258.5 \mu\text{A h cm}^{-2}$ ($\sim 2585 \mu\text{A h cm}^{-2} \mu\text{m}^{-1}$) and the reversible capacity in the first cycle is $106 \mu\text{A h cm}^{-2}$ ($\sim 1060 \mu\text{A h cm}^{-2} \mu\text{m}^{-1}$), resulting in an efficiency of 41 % from first to second cycle, and 44% over 150 cycles ($470 \mu\text{A h cm}^{-2} \mu\text{m}^{-1}$ Fig. 4a-b). Our 3D architecture TiO_2 film can deliver a capacity of $470 \mu\text{A h cm}^{-2} \mu\text{m}^{-1}$ over 150 cycles, and this value is about six order of magnitude higher as compared to layers of self-organized TiO_2 nanotubes with 600 nm ($80 \mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$) and 900 nm ($92 \mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$) lengths [6,7]. For TiO_2 annealed at 550 °C the total capacity in the first discharge is $105 \mu\text{A h cm}^{-2}$ ($\sim 1050 \mu\text{A h cm}^{-2} \mu\text{m}^{-1}$) and the reversible capacity in first cycle is $57.5 \mu\text{A h cm}^{-2}$ ($\sim 575 \mu\text{A h cm}^{-2} \mu\text{m}^{-1}$)

$^2 \mu\text{m}^{-1}$), resulting in an efficiency of 54 % from first to second cycle, and 28 % over 105 cycles. For TiO_2 at 700 °C the total capacity in the first discharge is $91.2 \mu\text{A h cm}^{-2}$ ($\sim 912 \mu\text{A h cm}^{-2} \mu\text{m}^{-1}$) and the reversible capacity in first cycle is $36.6 \mu\text{A h cm}^{-2}$ ($\sim 366 \mu\text{A h cm}^{-2} \mu\text{m}^{-1}$), resulting in an efficiency of 40 % from first to second cycle, and 38 % over 100 cycles. Achieving reversible reactions in the intercalation zone of anatase is possible in these films with 100 nm thickness due to the fact that their mesostructure (i.e. porous structure) is composed of interconnected pores of 4 – 5 nanometers in size within a 3D lattice. The mesostructure facilitates the diffusion of Li ions throughout the entire volume of the thin film, which clearly shows the importance of the correct development of the thin film mesostructure. Nevertheless, the wide voltage window (0.1 – 2.6 V) provides very high irreversibility (Fig. 3). In general, the efficiency from first to second cycle is very low ca. 35 – 37 % (Table 1). Lithium intercalation into trapped sites, side reactions of lithium with some H_2O molecules adsorbed on the TiO_2 [6,7,29], the formation of a very thin disordered layer at the electrode surface [9] and poor intrinsic electronic conductivity [30] are possible origins for the irreversible capacity. Gao et al.[31], reported the first direct evidence of new reaction mechanisms in amorphous TiO_2 nanomaterials, indicating that the lithiation started with the valence reduction of Ti^{4+} to Ti^{3+} leading to a Li_xTiO_2 intercalation compound. However, in this recent paper further intercalation of Li ions in TiO_2 triggered a transformation from amorphous to a crystalline phase identified as $\text{Li}_2\text{Ti}_2\text{O}_4$ with cubic structure [31]. On the basis of these observations, in our electrode prepared at 400°C, which gave an X-ray amorphous character, a plateau at 0.75 V is observed that may be assigned to the formation of very small crystallites of $\text{Li}_2\text{Ti}_2\text{O}_4$. This contribution is solely observed in the first discharge and consequently is not reversible

upon further charge/discharge (Fig. 3). This latter affirmation is in agreement with the observation of Xiong et al. [32], where they demonstrated the formation of a new crystalline material with a high degree of symmetry when cycling at potentials below 1.1 V which gave an irreversible crystallization process. In the crystallized product Ti and Li are randomly distributed among all octahedral sites in a nearly ideal cubic closed packed oxygen array. The resulting nanocrystalline product allows fast charge and discharge.

Up to now, little attention has been paid to avoiding the initial irreversibility in TiO_2 by using *pre-lithiation* treatment. Fig. 5 – 6 shows a comparison of the electrochemical performance with and without pre-lithiation treatment using new 1.0 – 2.6 V voltage ranges. Thus, efficiency from first to second cycle was increased to 52, 50 and 51 % for samples treated at 400, 550 and 700 °C, respectively. The pre-lithiated electrode showed much better cycling efficiency of 86, 75 and 85 % for samples at 400, 550 and 700 °C, respectively. A comparison between the cyclability of mesoporous electrodes with and without pre-lithiation treatment is depicted in Figure 7. The obtained capacities are lowered due to strict voltage limitation while the narrower voltage window allowed minimizing irreversibility as compared to the previous discussion. The best electrochemical behavior corresponds to electrodes thermally annealed at 400 °C, which precisely gave typical behavior of an anatase-based reaction. About 86 % of efficiency from first to second cycle with $19.65 \mu\text{Ah cm}^{-2}$ ($196.5 \mu\text{A h cm}^{-2} \mu\text{m}^{-1}$) and 90% of capacity retention over 100 cycles ($177 \mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$) are achieved. Capacities presented here for a 3D binderless mesoporous TiO_2 thin film are really attractive in terms of high kinetics and energy density when compared with other thin layer-based electrodes, for example, a titania nanotube layer grown on Ti foils

(13.5 and 13.2 $\mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$ recorded in 1st reversible and over 100 cycles, respectively), on Ti foams (63.3 and 66.7 $\mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$ recorded in 1st reversible and over 100 cycles, respectively) [33] or even comparing with highly ordered anodic TiO₂ nanotube arrays (26.7 $\mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$) [34] or a layer of ntTiO₂ containing submicron Co₃O₄ particles (137.3 $\mu\text{Ah cm}^{-2} \mu\text{m}^{-1}$) [35] suggesting that the novel architecture electrode presented here can be a potential candidate for the fabrication of nanostructured thin film microbatteries. To see further details of capacity value of different electrodes see Table 1.

In order to achieve extended cycle life in advanced electrodes the stability of the binderless TiO₂ thin films was studied. Ex-situ analysis of cycled electrodes prepared at 300 and 700 °C after 125 and 100 cycles at 3.0 V, respectively, were performed by HRTEM and SEM (Fig. 8). The mesoporous structure disappeared in both samples as deduced from HRTEM images from Fig. 7a,b. In this way, the pores seem to have disappeared and particles start coalescing. From TEM images it is observed that the agglomeration of particles is more evident for sample at 300 °C than for that of 700 °C. Using ex-situ SEM images we have detected that the obtained material after long cycling displays agglomerates (Fig. 7c,d) composed of almost spherical particles. The sample at 300 °C seems to exhibit large number of particles forming agglomerates where the porous structure seems to disappear, while the sample at 700 °C seems to be formed smaller particle agglomerates (about 20 nm) and some porous organization is observed with an average pore of 60-70 nm. This rearrangement does not compromise cycle life and capacity retention. Irrespective of the above discussed morphological changes, the initial cohesion and accessibility to the electrolyte of the initial domains in

the mesoporous structure are preserved, thus allowing extended cycling at moderate rates.

The half-cell using 100 nm TiO_2 layer is able to provide about 75 % of theoretical capacity in 900 s (3 C). Moreover, an ideal full 3-D, Li-ion battery combining this electrode with a 4.8 V cathode (e.g. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ or LiCoPO_4), could give a maximum energy density of $570 \mu\text{Wh cm}^{-2} \mu\text{m}^{-1}$ and power density of $2.54 \text{ mW cm}^{-2} \mu\text{m}^{-1}$. The values presented here are very interesting from the point of view of microdevices applications, in which high energy densities are mandatory.

4. Conclusions

In order to improve the performance of mesoporous titania in lithium microbatteries, TiO_2 films of ca. 100 nm with a well-defined hexagonally ordered porous structure were prepared directly on a titanium substrate. A strict control of voltage window and pre-lithiation treatment could drastically improve cycling efficiency. Maximum capacity values over 100 cycles of $470 \mu\text{A h cm}^{-2} \mu\text{m}^{-1}$ and $177 \mu\text{A h cm}^{-2} \mu\text{m}^{-1}$ are obtained for voltage ranges of 0.1 – 2.6 V and 1.0 – 2.6 V, respectively. For comparative purposes, films with 600 nm and 900 nm were also tested, although the capacity was significantly lower. Thus the porosity of this material allows the electrolyte reaching the complete mass of the electrode, while its mechanical stability allows tackling the use of polymer binder, and the electrical contact with the current collector makes unnecessary the use of carbon additives. All of these effects result in a higher overall areal and volumetric capacity than in other TiO_2 -based anode material previously considered for microbatteries.

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Table 1. A comparison of the reversible and irreversible capacities obtained of the different mesoporous TiO₂ electrodes. Note that “TC” is the total capacity in first discharge, “IC” is the irreversible capacity from first to second cycle, “RC” is the reversible capacity measured in second cycle, and “PL” is a pre-lithiated electrode.

TiO ₂	Voltage window	TC / $\mu\text{Ah cm}^{-2}$	IC/ $\mu\text{Ah cm}^{-2}$	RC / $\mu\text{Ah cm}^{-2}$	Efficiency / %
300°C	0.1-2.6	176	111	65	37
400 °C	0.1-2.6	258.5	152.5	106	41
	1.0-2.6	59.9	28.8	31.1	52
	1.0-2.6 PL	23	3.2	19.8	86
550 °C	0.1-2.6	105	47.5	57.5	54
	1.0-2.6	42.2	20.94	21.26	50
	1.0-2.6 PL	26.5	6.7	19.8	75
700 °C	0.1-2.6	91.2	54.6	36.6	40
	1.0-2.6	37.5	19.2	18.3	51
	1.0-2.6 PL	15.6	2.3	13.3	85

Figure caption

Figure 1. X-ray diffraction patterns of binderless mesoporous TiO₂ thin films fabricated by protocol (1) on Ti plates (0.5 mm and 99.6%+ purity) at 300 °C under vacuum and annealed at 400, 550 and 700 °C in air, respectively.

Figure 2. HRTEM micrographs of (a) as-synthesized TiO₂ thin film grown on Ti by synthesis protocol (1), (b) As-synthesized TiO₂ thin film grown on Ti by synthesis protocol (2), (c) calcined TiO₂ thin film (300°C under vacuum) grown on Ti by synthesis protocol (1), and (d) calcined TiO₂ thin film (300°C under vacuum) grown on Ti by synthesis protocol (2).

Figure 3. Galvanostatic discharge/charge curves vs. capacity of binderless 3D mesoporous TiO₂ thin films prepared by protocol (1) obtained at 300 °C under vacuum and annealed at 400, 550 and 700 °C in air. Current rate: 5 $\mu\text{A cm}^{-2}$. Voltage limits: 2.6 – 0.1 V.

Figure 4. Reversible capacity (areal and volumetric) vs. cycle number in lithium micro-cells for binderless 3D mesoporous TiO₂ thin films prepared by synthesis protocol (1) obtained at 300 °C under vacuum and annealed at 400, 550 and 700 °C in air, respectively. Voltage window: 0.1 – 2.6 V.

Figure 5. Galvanostatic discharge/charge curves vs. capacity of binderless 3D mesoporous TiO₂ thin films using 1.0 – 2.6 V voltage windows.

Figure 6. Effects of pre-lithiation treatment on lithium (de)-insertion on the binderless 3D nanoporous TiO₂ thin film electrodes.

Figure 7. A comparison of electrochemical cycling performance of binderless 3D mesoporous TiO₂ thin films electrodes with (a) and without pre-lithiation treatment (b). Voltage window: 1.0 – 2.6 V.

Figure 8. Ex-situ HRTEM (a and b) and SEM (c and d) images of cycled electrodes prepared at 300 and 700 °C after 125 and 100 cycles at 3.0 V, respectively.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Graphical Abstract

Ordered mesoporous oxide for thin film microbatteries with enhanced lithium storage

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Highlights

- 3D ordered mesoporous binderless TiO₂ electrode exhibited improved Li storage.
- The hexagonal packing accounts for a better connectivity and lithium diffusivity.
- Maximum capacity of 470 $\mu\text{A h cm}^{-2} \mu\text{m}^{-1}$ over 100 cycles is achieved.