Contents lists available at ScienceDirect

Electrochimica Acta

ELSEVIER



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The double-walled nature of TiO₂ nanotubes and formation of tube-in -tube structures – a characterization of different tube morphologies



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ARTICLE INFO

Article history: Received 12 December 2016 Received in revised form 3 February 2017 Accepted 16 February 2017 Available online 20 February 2017

Keywords: Double-walled nanotubes single-walled nanotubes tube-in-tube configuration Thermo-Gravimetric Analysis Differential Scanning Calorimetry

1. Introduction

One-dimensional (1D) nanostructures, in particular in the form of nanotubes (NTs), provide an exceptional combination of optical, electrical and chemical properties with a distinct and defined geometry and represent, therefore, ideal arrays for application in fields such as energy conversion and storage, and medicine [1–3].

Several methods are reported for the synthesis of 1D TiO_2 nanotubes, such as hydrothermal, sol-gel or template-assisted approaches [4–6]. The most common and straightforward is self-organizing electrochemical anodization (SOA) [3,7,8].

Traditionally, anodization is carried out in a simple twoelectrode configuration, where the metal of interest (M, the anode) under a suitable voltage is oxidized ($M \rightarrow M^{z+} + ze^{-}$) and converted to the corresponding (mostly compact) metal oxide, by a reaction with O^{2-} ions derived from H₂O in the electrolyte [3].

For an optimized set of experimental parameters (*e.g.*, electrolyte composition and pH, temperature, applied voltage, time *etc.*), self-organizing conditions can be established and one-

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http://dx.doi.org/10.1016/j.electacta.2017.02.094 0013-4686/© 2017 Elsevier Ltd. All rights reserved.

ABSTRACT

In the present work we show how to achieve different nanotube morphologies (namely, not only singleand double-walled tubes, but also a tube-in-tube configuration) by combining specific anodization parameters. We characterize as-grown tube layers in terms of morphology, chemical composition and properties. As-grown tubes exhibit a double-walled morphology, that is, they consist of an inner and an outer shell. The low quality inner shell can be removed by an optimized chemical treatment thus leading to nanotubes of a higher quality oxide and with a single-walled nature. Double-walled tubes grown at low electrolyte temperature provide a thick inner shell that after adequate annealing can form a unique tubein-tube morphology.

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dimensional TiO₂ NTs can be grown as highly aligned, sizecontrolled, and back-contacted (*i.e.*, anchored to a metallic substrate) nanostructure arrays. These arrays provide a broad range of functionalities and properties *e.g.* for a use in solar cells [9,10], as well as in photo-electrochemical [11], energy storage [12] and biochemical devices [13]. Key to the formation of nanoporous/ nanotubular oxide arrays is the presence of F^- ions in the electrolyte that, under optimized conditions, establishes a steady-state equilibrium between oxide formation and dissolution required for self-organization [14,15].

Since the first demonstration of self-ordered anodic TiO_2 nanostructures by anodization [16], tremendous research on the structural design and properties of anodic TiO_2 tubes has been carried out.

The first generation of anodic TiO₂ NTs was grown in acidicaqueous solutions [16–18]. For these tubes, only a limited maximum length ($\sim 2.5 \,\mu$ m, due to high chemical etching rate promoted by excess water) and a low self-ordering degree (ripplewalled tubes were typically reported) could be achieved.

The introduction of organic electrolytes represents a keystone in the growth of smooth, ordered and longer (up to several 100 μm) TiO_2 nanotubes [19]. Among organic electrolytes, most classic are glycerol and the nowadays widely used mixtures of

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ethylene glycol (EG) containing ammonium fluoride (NH₄F) and low amounts of water (~ 1–5 vol%). Tubes grown in these electrolytes – due to the growth mechanism – typically feature a double-walled (DW) structure, with an inner (shell) wall rich in carbon-species embedded from the electrolyte during the anodic growth, while an outer shell of nearly pure TiO₂ is present [20–22].

Owing to its composition [22], the inner shell is notoriously detrimental for TiO_2 NT applications *e.g.* as photo-anode in solar cells and photo-electrochemical devices, among others, as carbon retards the electron mobility .

Most recent findings show that a simple chemical treatment in combination with low-temperature annealing can selectively etch out the inner part of DW NTs leaving behind a so-called single-walled (SW) nanostructure; as a result, SW tubes typically have larger inner diameter, a smoother and better-defined wall surface and, most notably, improved electronic properties compared to the original DW tubes [22].

A most remarkable step-forward in the fabrication of TiO_2 nanotubes has been achieved through the introduction of weak organic acids (*e.g.*, lactic acid (LA), glycolic acid, citric acid, and EDTA) in the traditional EG-based electrolyte. By preventing the occurrence of dielectric breakdown events in the growing oxide, these additives allow anodization at a significantly higher voltage, ultimately yielding a ultra-fast growth that drastically (positively) affects the tubes' properties. Specifically, while preserving a double-walled morphology, EG/LA-TiO₂ NTs exhibit a larger diameter, superior mechanical resistance, and improved robustness, compared to classic EG-tubes. All these features contribute to an amelioration of the performance of such nanotubes in several applications [22–25].

In spite of the wide use of DW-TiO₂ NTs fabricated in EG/LAbased electrolytes, their structural and chemical properties as well as their differences to SW tubes have only sparingly been investigated. Moreover, no study on the effect of different anodization conditions, also combined with specific post-growth treatments, on the morphology of such tubes has been reported so far.

Thus, within this work, we investigate the effect of anodizing temperature on the growth of EG/LA-based TiO_2 nanotubes, and characterize composition, structure and differences in properties of such tubes.

In particular, we find that, for tubes grown in EG/LA electrolyte using low anodizing temperatures, a significant thickening of the NT walls is observed; this then represents a precursor state to form a remarkable tube-in-tube (T-in-T) morphology that develops during an annealing treatment.

2. Experimental

2.1. Preparation of TiO₂ nanotubes

TiO₂ nanotubes (16 μ m-long) were grown on titanium foils (0.125 mm thick, 99.6+ % purity, Advent, England) that, prior to anodization, were degreased by sonication in acetone, ethanol and isopropanol, rinsed with deionized water, and then dried with a nitrogen jet. Electrochemical anodization was performed with a high-voltage potentiostat (Jaissle IMP 88 PC) at 120 V in a two-electrode configuration with a Pt foil as counter electrode, and using an electrolyte composition of 1.5 M lactic acid (LA, DL-Lactic acid, ~90%, Fluka), 0.1 M ammonium fluoride (NH₄F) and 5 wt % deionized H₂O in ethylene glycol (99 vol %) [23].

Anodization was carried out at two different temperatures, namely room temperature (RT) and 10 °C (set with a HAAKE F3 Thermostat). In particular, 16 μ m-long tubes were grown in 10 min for anodizing at RT, while much longer time (1 h 30 min) was needed to obtain comparably long tubes at 10 °C.

After anodizing, the samples were washed in ethanol and dried in a nitrogen stream.

Thereafter, a chemical dissolution procedure was used to selectively dissolve the low-quality tube inner shell [22], that is, converting DW tubes to a SW morphology.

For this, RT-nanotubes were first annealed in a Rapid Thermal Annealer (Jipelec JetFirst100) at $150 \,^{\circ}$ C for 1 h in air, at a heating and cooling rate of $30 \,^{\circ}$ C min⁻¹. Afterwards, tubes were dipped in a piranha solution (H₂SO₄: H₂O₂ = 3: 1) for 6 min at 70 $\,^{\circ}$ C, then washed in H₂O and EtOH, and finally dried with a nitrogen jet.

Some of the fabricated tube layers (prepared either at RT (both single- and double-walled tubes) or at $10 \,^{\circ}$ C) were annealed in a Rapid Thermal Annealer at 450 $^{\circ}$ C in air for 1 h, with a heating and cooling rate of 30 $^{\circ}$ C min⁻¹.

2.2. Material physico-chemical characterization

For morphological characterization, a field-emission scanning electron microscope (FESEM, Hitachi SEM FE 4800) was used. The thickness of the nanotubes was measured from SEM cross-section images.

X-ray diffraction (XRD), performed with an X'pert Philips MPD (equipped with a Panalytical X'celerator detector) using graphite monochromized Cu K α radiation (λ = 1.54056 Å), was used to analyze the crystallographic properties of the materials.

HRTEM images were obtained using a HRTEM TITAN 60–300 microscope with an X-FEG type emission gun, operating at 300 kV. This instrument is equipped with a Cs image corrector and a STEM/ HAADF detector; its point resolution is 0.06 nm in the TEM mode. The elemental mappings were obtained by STEM/EDS technique, with an acquisition time of 20 min.

Composition and chemical state information were obtained by Energy Dispersive X-ray (EDX) and by Scanning Auger Nanoprobe (PHI 710 – Physical electronics, US; accelerating voltage 20 kV, current 1 nA).

High spatial resolution scanning Auger Electron Spectroscopy (AES, Physical Electronics PHI 700Xi Scanning Auger Nanoprobe) was employed to investigate the compositional variations along the TiO_2 nanotube length.

Thermogravimetric analysis (TGA) coupled to Mass Spectrometry (MS) (Netzsch STA 409 CD, equipped with a Skimmer QMS 422 mass spectrometer (MS/EI)) was carried out to study the thermodynamic behavior of the samples. TiO₂ nanotubes (around 10 mg) were detached from Ti metal foil by physical bending of the substrate. TGA-MS was scanned from room temperature (RT) to 650 °C, with a 10 °C/min ramping rate, in air. To remove contaminations, helium was purged before any measurement.

Fourier Transform Infrared spectroscopy (FTIR; Thermo Fisher FTIR6700) was carried out with a microscope attached to a FTIR6700 bench. FTIR spectra were collected from a *ca.* 100 μ m-large spot.

Differential Scanning Calorimetry (DSC, Perkin Elmer) was used to measure the crystallization temperature of the investigated samples. TiO₂ nanotubes (\sim 10 mg) were first detached from the Ti metal foil by physical bending of the substrate; spectra were collected in a N₂ atmosphere and the temperature was scanned from 25 °C to 400 °C, with a 10 °C/min ramping rate.

3. Results and Discussion

Nanotube layers, as shown in Fig. 1, were fabricated in an organic-based electrolyte (0.1 M $\text{NH}_4\text{F}-5 \text{ wt.\%}$ $\text{H}_2\text{O}-\text{EG}$), also containing lactic acid (1.5 M).

This electrolyte was selected as lactic acid is reported to shift the "burning" voltage to a significantly higher value [26] and, thus, allows a high ion flux through the oxide film and therefore



Fig. 1. (a-i) SEM top-view (first two columns) and cross-sectional (third column) images of (a-c) double-walled NTs, (d-f) single-walled NTs obtained from DW tubes after mild annealing and chemical etching, and (g-i) tube-in-tube fabricated by anodizing at 10 °C. In particular, the first column shows amorphous samples, while the second and third columns report crystalline samples. (j) Current-time behavior for anodization at 120 V in LA electrolyte at room temperature (black-curve) leading to a double-walled morphology, and at 10 °C (red curve) resulting in a tube-in-tube morphology after annealing.

provides an extremely fast growth of the anodic oxide without affecting the tubes' functional properties [23,27,28]. Fig. 1(j) shows the current density (*j*) vs. time characteristics at an anodization voltage of 120 V, with LA in the electrolyte, and for anodizing at room temperature (RT, black curve) and at 10 °C (red curve). For tubes grown at 10 °C, after an initial short stage which corresponds to the formation of a compact oxide at the metal/electrolyte interface, *j* drops to a steady value with continuous tube growth (as typically occurs in optimized self-organizing systems) [29]. In the RT case, a steep rise in *j* is observed; this is caused by Joule-heating induced temperature increase that in turn accelerates the tube growth. In line with this, anodizing in EG/LA electrolyte at room temperature leads to 16 μ m-thick nanotube layers in 10 min – remarkably, anodization time longer than 2 h is typically required

to grow comparably long $\rm TiO_2$ NTs in traditional EG-based electrolytes with no lactic acid [23].

As shown in Fig. 1 (a-c), TiO_2 nanotubes grown under these conditions are double-walled nanotubes that consist of two different types of oxide, namely an outer shell (OS) of comparably pure TiO_2 , and an inner shell (IS) that is mainly composed of carbon-rich titanium oxide or oxy-hydroxide and that forms due to electrolyte uptake during anodization [20–22].

Despite a clear difference in quality and composition, the outer and inner shells of DW nanotubes can only vaguely be distinguished from SEM in as-grown layers (Fig. 1 (a)).

However, annealing of the DW NTs leads to a separation of IS and OS into two distinct layers; in detail, the outer part of the wall (OS) remains compact, while the inner wall (IS) becomes porous (Fig. 1 (b,c)). This is an indication that carbon-trapped species (hydrocarbon compounds) are mainly in the IS, and being "burned-off" and evaporated as CO_2 during annealing produces the observed porosity – in line with literature [30].

De-coring of the DW tubes of Fig. 1(a) as described in the experimental section leads to single-walled nanotubes (Fig. 1 (d)) that exhibit both a thinner wall and a wider inner diameter (\sim 20 nm and \sim 95 nm, respectively).

These results were obtained after optimizing the experimental conditions of the de-coring (etching) process, namely the immersion temperature and time to 70 °C and 6 min, respectively. For longer etching (and/or higher temperatures) the resulting dissolution of the OS significantly affects the morphology and, eventually, the TiO_2 nanotubes peel off from the Ti substrate.

Annealing of single-walled tubes (*i.e.*, consisting of only the OS) does, in contrast to the DW tubes, not affect the morphology of the layer as observed in SEM (Fig. 1(e,f)) and reflects the high quality (and thermal resistance) of the oxide.

As shown by XRD patterns in Fig. 2a, as-formed tubes are amorphous and annealing under most classic conditions for EGbased tubes (450 °C, 1 h in air) leads to the crystallization of both DW and SW layers in the form of anatase, with only a small contribution from rutile (Fig. 2(b)). In line with previous reports, from XRD no clear difference between the crystallinity of DW and SW tubes can be observed – however, in literature, TEM investigation showed larger average crystallite sizes in singlewalled NTs [20].

In the present work we used an extended range of characterization techniques to gain information on the chemical compositions of double- and single-walled tubes, as described below.

Energy Dispersive X-ray measurements indicate that as-formed DW tubes exhibit a content of carbon higher than that of single-walled NTs (*i.e.*, ~ 7.5 at% and ~ 5.5 at.% respectively, Fig. 3(a)), this being attributed to the presence of the inner tube shell in the double-walled morphology; similar amounts of F were observed in both DW and SW – that is, F^- is mainly in the outer layer and originates from anodizing in the presence of fluorides (here, NH₄F).

More detailed investigations were carried out on ion-milled cross-sections of amorphous tubes. Fig. 3(b,c) shows the line scans of titanium, fluoride and carbon collected through Scanning Auger Electron spectroscopy and superimposed on the original SEM images of the different tube morphologies.

In line with a double-layered morphology, C distribution in DW structures is higher in the inner walls of the tubes. On the other hand, Ti and F concentrations drop inside the tubes, with F-rich

regions corresponding to C-depleted regions (and vice versa) [23,31].

In particular, AES of DW structures points out that the concentration of F is highest in the outermost part of the outer layer, in line with a comparably higher concentration of F^- inbetween tubes. This is in line with earlier findings and anodic tube formation mechanism that lead to a fluoride-rich layer at tube bottoms and outer walls during nanotube growth [31,32].

In SW tubes, Ti and C concentrations reach their local maxima in the walls (OS) and decrease inside the tubes (Fig. 3(c)); this confirms the removal of the carbon-rich shell by chemical etching in piranha solution [20,21,30].

High-angle annular dark field scanning TEM (HAADF-STEM) and elemental mapping of amorphous DW tubes (Fig. 4(a)) show a distribution of C, F and TiO in line with that revealed by AES: carbon-species (from electrolyte uptake) mainly concentrate in the inner tube shell, while the amounts of fluoride and titanium (oxide or oxy-hydroxide) are higher towards the tubes' outer walls.

HAADF and TEM mappings of SW tubes in Fig. 4(b) confirm the removal of the inner shell after chemical etching, with a consequent significant decrease of the wall overall thickness. Moreover, C (intrinsic residues), F and TiO species are homogeneously distributed in the remaining outer shell.

For anodization performed at 10 °C, a significantly longer time (1 h 30 min vs. 10 min at RT, Fig. 1(j)) was needed to grow 16 μ m-long nanotubes (Fig. 1 (g)); that is, the nanotubes' growth rate decreases by a factor of 9.

This is mainly ascribed to the lower anodizing temperature that influences the kinetics of ion migration through the oxide, as well as the solubility of the reaction products in the electrolyte. A combination of these factors causes a two-fold effect: i) Ti^{4+} , O^{2-} and F^- migration (key to a steady-state oxide formation/dissolution equilibrium for self-organization) is slowed down – hence, longer anodization time is clearly needed, but also ii) the solubility of Ti hydroxides, oxy-hydroxides and C-enriched compounds (embedded from the electrolyte) is reduced [33,34].

Therefore, under such conditions, an overall significant thickening of IS is observed, as shown in Fig. 1(g), and Ti-C based compounds (formed by reaction of carbon residues and precipitated Ti ions ejected from the growing oxide) accumulate in the IS.

From Fig. 1(g), as-formed tubes grown at 10 °C show \sim 80 nm-thick walls and an inner diameter of \sim 30 nm, while those prepared at RT have \sim 45 nm-thick walls and a \sim 55 nm inner diameter.

For these tubes, after annealing at 450 °C in air, a remarkable tube-in-tube morphology as shown in Fig. 1(h,i) becomes



Fig. 2. XRD patterns of (a) amorphous and (b) crystalline DW, SW and T-in-T layers.



Fig. 3. (a) C and F contents of the investigated layers, determined by EDX measurements; (b–d) High resolution Auger Electron Spectroscopy (AES) horizontal scans of different elements (Ti, C and F) recorded with as-formed TiO₂ nanotube layers.

apparent. The tube wall thickness is reduced (*i.e.*, from \sim 80 nm to \sim 48 nm) and an additional inner tubular structure is formed.

Elemental composition of the as-formed precursor tubes (*i.e.*, T-in-T(prec) that after annealing become tube-in-tube structure) by EDX (Fig. 3(a)) shows that T-in-T(prec) exhibit the highest content of carbon and also of fluoride species (*i.e.*, 10 at% and \sim 7 at%, respectively,), in line with the proposed mechanism based on increased ion accumulation in the IS at low anodization T.

Concentration scans of fluoride, titanium and carbon obtained by scanning AES and superimposed on the ion-milled SEM image of T-in-T(prec) in Fig. 3(d) are also in line with the above scenario. That is, the distributions of Ti and F appear nearly uniform throughout the nanotubes, while that of C is higher inside the tubes, thus confirming the accumulation of a carbon-rich Ti-based layer in the tubes' inner shell [33,34], due to the low solubility of the IS at $10 \,^{\circ}$ C.

TEM mappings of T-in-T(prec) (Fig. 4(c)) confirm a nearly homogeneous distribution of C, F and TiO in the tube walls, and a comparison of the HAADF-STEM images of all the as-formed samples (Fig. 4(a-c)) clearly highlights that overall the thickness of NT walls follows the order T-in-T(prec) > DW > SW.

Moreover, a comparison of the fluoride distribution and content in T-in-T before and after annealing (*i.e.*, T-in-T(prec) vs. T-in-T (ann)) at 450 °C (Fig. 5(a,b)) shows a lower F content in the

(a) Double-walled



(b) Single-walled







Fig. 4. High Angle Annular Dark Field Scanning TEM (HAADF-STEM) images and C, F and TiO elemental mappings of (a) DW, (b) SW and (c) T-in-T(prec) TiO₂ NTs. All samples are amorphous.

annealed sample suggesting that the fluoride accumulated inside the tubes (Fig. 3(d)) is partially removed during the thermal treatment. This may be attributed to the sublimation of TiF_x compounds that typically occurs at T ~ 290 °C [35].

In line with this, EDX of crystalline T-in-T (Fig. 3(a), T-in-T(ann)) shows that F and also C contents drastically drop to $\sim 2-4$ at.% (that is, the level of environmental contamination) [22], and the TEM

image in Fig. 5(c) clearly shows the appearance of an inner tube and of empty space after annealing the T-in-T(prec).

The compositional and structural changes associated with the annealing process in DW, SW, and T-in-T(prec) were followed using Thermo-Gravimetric Analysis, coupled with Mass Spectrometry (TGA-MS); the characteristic T-dependent decomposition patterns are shown in Fig. 6.



Fig. 5. F elemental TEM mappings of (a) as-formed and (b) crystalline T-in-T TiO₂ NTs. (c) HRTEM of a T-in-T nanotube formed after annealing.



Fig. 6. Thermal desorption profiles for m/e = 18 (H₂O) and m/e = 44 (CO₂) measured by Thermo-Gravimetric Analysis coupled with Mass Spectrometry (TGA-MS) for (a) double-walled, (b) single-walled, (c) T-in-T layers. (d) Comparison of the CO₂ evolution peaks measured for the three different layers.

 $A \sim 2-3$ wt% loss (corresponding to a mass/charge (m/e) = 18) is observed in all the three layers at T $\sim 250 - 300$ °C, that may be ascribed to the desorption of disproportionated H₂O from the hydroxylated Ti surface sites [36].

 CO_2 from TiO₂ surface typically occurs at room temperature (or below) [37,38]. Therefore, it is plausible that the carbon loss observed by TGA at such higher temperatures corresponds to the pyrolysis of some C-based contaminants in all the three NT layers.

Different responses for the three tubular layers are observed for a mass/charge loss of 44 (*i.e.*, corresponding to CO_2), in the range of T \sim 380–390 °C. It is reported that desorption of environmental

In particular, the lowest weight loss ($\sim 5 \text{ wt\%}$, Fig. 6(b)) is observed for single-walled tubes; in this case, carbon loss is assigned to the combustion of some contaminants from the tube

outer shell that remain also after de-coring DW tubes and that can be removed from SW tubes only when annealing at T $\sim400\,^\circ\text{C}$ or higher [20,22].

Higher amounts of carbon (*i.e.*, $\sim 8-9$ wt%, Fig. 5(a,c)), in line with data from EDX (Fig. 3(a)), are "burned-off" in double-walled and tube-in-tube NTs. Here, the contribution is dominated by the thermal oxidation of carbon species embedded in the tube inner walls (see above) [20]. Moreover, the larger amount of CO₂ from T-in-T with respect to DW supports the proposed mechanism of wall thickening at low anodization T due to reduced ion solubility and electrolyte ion uptake.

A most significant difference in the CO_2 peak for the three tube configurations is reported in Fig. 6(d).

It is clear that the combustion of C species in DW and T-in-T tubes occurs at a lower temperature than in SW; this, together with a sharper peak profile than in the SW case, indicates a possible different nature of carbon compounds in the structures.

FTIR spectra collected for as-formed DW, SW and T-in-T, and reported in Fig. 7(a) confirm the presence of OH- and of C-based moieties on the surface of the three types of nanotubes.

In all the three cases, the peaks at $1620-1630 \text{ cm}^{-1}$ and the broad peaks at $3100-3600 \text{ cm}^{-1}$ are assigned to the bending and stretching modes, respectively, of hydroxyl groups while the small peak at 3700 cm^{-1} indicate a minimum of free water molecules [39]. In particular, the broad band at ~ 3300 cm^{-1} and the relatively sharper bands at ~ 1650 cm^{-1} can be assigned to the OH stretching and the HOH bending modes of free water, respectively [40], while the peaks in the $3400-3600 \text{ cm}^{-1}$ range correspond to -OH groups weakly bound to uncoordinated Ti surface sites, as also observed during TGA measurements (Fig. 6) [41].

For DW and T-in-T structures well defined peaks appear at 2840–3000 cm⁻¹ corresponding to alkyl $-CH_2$ and -CH stretching bonds [40] likely due to EG/LA residues. Accordingly, the intensity of the carbon-associated vibration modes in single-walled NTs is significantly lower compared to that of the other two structures (DW and T-in-T tubes) [42,43].

Finally, the vibrational modes associated to environmental CO_2 adsorption ($\sim 2340 \text{ cm}^{-1}$) appear in all three as-formed layers [44,45].

Additional FTIR spectra (Fig. 7(b)) have been collected to identify differences in as-formed (i) traditional DW tubes (DW (ref)), (ii) DW tubes with (purposely unremoved) electrolyte

remnants (*i.e.*, no washing-step in EtOH after anodization – DW(no EtOH)), and (iii) DW tubes before etching treatment (DW (Ann150)). The origin of C-contamination is of primary concern.

All the DW layers exhibit similar FTIR spectra, both in terms of band positions and relative intensities.

A most relevant aspect is the similar surface compositions of DW(ref) and DW(no EtOH) layers: this confirms that C content in DW structures is not the result of plain electrolyte residues in the oxide tubes – in this case, washing in EtOH would have removed this contribution at least partially, and DW(ref) and DW(noEtOH) spectra would exhibit different features.

Moreover, a C content (from the peak relative intensities) that follows the trend DW(Ann150) \sim DW(ref) > SW (Fig. 7(a,b)) confirms that (i) mild annealing at 150 °C before the chemical etching treatment does not affect the C contained in DW tubes (DW (Ann150) \sim DW(ref)) and (ii) the main contribution to the overall carbon content comes from the inner shell (DW(ref) > SW).

Information on thermally-induced transitions (namely, crystallization) in DW, SW and T-in-T(prec) structures was obtained from Differential Scanning Calorimetry measurements (Fig. 8(a)).

Noteworthy, data from DSC are complementary to those from TGA: the thermogravimetric analysis provides information on mass variation (*e.g.*, due to dehydration and combustion processes) occurring in a material heated up to a certain T; on the other hand, DSC shows the material response to a temperature variation in terms of lattice rearrangement [46].

In particular, DSC peaks as those reported in Fig. 8(a) indicate that the material undergoes crystallization, with the T of maximum heat flow representing the crystallization temperature (T_c). Typically, the most intense the DSC peaks, the fastest is the associated reaction – that is, the less defective the material.

Fig. 8(a) shows that not only single-walled nanotubes exhibit the lowest crystallization temperature, but also feature the sharpest and most intense peak; in line with previous discussion, both characteristics prove the high-quality oxide composition of the outer tube shell and indicate that the amorphous-into-crystalline transition in SW tubes is already achieved at T_c as low as ~ 356 °C.

By contrast, both DW and T-in-T tubes undergo crystallization at higher temperatures (*i.e.*, $T_c = ca$. 363 and 375 °C, respectively), and the broadening of the associated DSC peaks suggest that parallel processes occur in combination with crystallization.



Fig. 7. (a) FTIR spectra of as-grown SW, DW and T-in-T tubes. (b) FTIR spectra of conventional as-formed DW TiO_2 NTs (DW(ref)), of DW tubes annealed under mild conditions (DW(Ann150)), and of as-formed DW tubes without the washing-step in EtOH typically performed after anodization (DW(no EtOH)).



Fig. 8. (a) Differential Scanning Calorimetry curves of SW, DW and T-in-T tubes. (b) DSC spectra recorded for conventional as-formed DW TiO₂ NTs (DW(ref)), of DW tubes annealed under mild conditions (DW(Ann150)), and of as-formed DW tubes without the washing-step in EtOH typically performed after anodization (DW(no EtOH)).

In particular, T_c values of DW and T-in-T tubes are in the same temperature range as that of carbon (hydrocarbon) species combustion to CO_2 determined by TGA (Fig. 6(d)).

It is thus plausible that the large amount of carbon accumulated in DW and T-in-T tubes retard the crystallization of the tubes.

By contrast, the T_c value of SW tubes is clearly lower than the temperature for CO_2 release from such structures (Fig. 6(b)), indicating that carbon remnants in the outer shell of tubes do not affect the crystallization process. Nevertheless, it should be mentioned that F^- is known to facilitate the amorphous-to-crystalline transition of TiO₂ [47]. Therefore, a contribution of fluoride coating on the OS (Fig. 4(b)) to the lowering of the crystallization temperature for SW structures cannot be excluded.

The different responses to T variation of the three NT types confirm the different origins and properties of C-based species and further highlight the close similarity between DW and T-in-T precursor structures.

DSC characterization of the additional DW(no EtOH) and DW (Ann150) nanotube layers (Fig. 8(b)) is also in line with the above results: the similar peaks obtained with the three different double-walled NT samples show that the retarded crystallization process should be solely attributed to the intrinsic composition of the IS in the double-walled structures, with no contribution from adsorbed electrolyte species.

Most important, results in Fig. 8(b) confirm that only chemical etching of DW tubes under optimized conditions can lead to the recovery of properties and chemical composition that are typical of higher-quality TiO_2 , by removing the poor-quality C-enriched inner shell.

3.1. Origin of the tube-in-tube morphology

A most remarkable key-aspect, pointed out by above results, is that, although annealing of DW and T-in-T(prec) structures leads to two clearly different morphologies, namely the formation of selfstanding inner tubes in the T-in-T case, all the characterizations carried out show for the precursor to a tube-in-tube morphology a similar chemical composition as for DW tubes. Also after annealing, it becomes evident the distinct nature of outer and inner shells – that is, a double-walled morphology clearly appears.

In particular, EDX measurements and TEM elemental mappings (Fig. 3 and 4) showed that double-walled and tube-in-tube layers not only feature comparable chemical composition (*i.e.*, both contain C (and F) species accumulated from the electrolyte), but these species have also similar distribution profiles within the tubes as, in both cases, they were shown to accumulate in the inner shell.

Moreover, TGA and DSC results indicated that owing to the peculiar composition of their double-walled structure, dehydration and combustion processes occur when heating the layers (more precisely, they occur at a larger extent than in SW tubes) and, most important, showed that the presence of significant amounts of C retards the crystallization process.

A most relevant (and only) difference between amorphous DW and T-in-T is, therefore, the relatively larger thickness of the T-in-T walls. The higher thickness of the IS is a result of anodizing at a low temperature – this being particularly evident from the SEM images in Fig. 1.



Fig. 9. Effect of different annealing temperatures on the inner/outer shells' separation in tube-in-tube layers: (a) 250 °C, (b) 350 °C, and (c) 450 °C.

Therefore, also in line with previous studies [33,34], one can conclude that the same anodic mechanism is at the basis of both DW and T-in-T(prec) growth, and one must ascribe the origin of the peculiar tube-in-tube configuration to a temperature-induced effect on the thicker wall.

Annealing of DW and T-in-T(prec) leads to some porosification of the inner shell (see SEM images of Fig. 1(b,c)), due to the sublimation/evaporation of IS carbon residues burned-off as CO_2 at sufficiently high temperature (~ 400 °C, Fig. 6(a)).

However, in T-in-T precursor structures the IS contracts to a larger extent than in DW tubes and generates a physical separation of the inner shell from the outer shell, leading to the appearance of clear self-standing inner tube (Fig. 1(h,i)).

This is fully supported by the SEM images in Fig. 9(a-c) for T-in-T(prec) tubes annealed at different temperatures, in the 250–450 °C range: for low annealing temperature (250 °C, Fig. 9(a)) no clear morphological changes are observed in the T-in-T structure, also in line with TGA data – Fig. 6(c) clearly shows that at such T only H₂O desorption from tube walls occurs (that is, no effect on carbon contaminations is observed).

However, for $T \ge 350$ °C carbon-based species in the tubes are burned-off as CO₂ and the inner and outer shells separate to an extent that is proportional with the annealing temperature (Fig. 9(b,c)) – this suggests that a temperature-dependent mechanical stress is generated during annealing [48] due to the loss of CO₂ which in the case of the thinner DW tube can be accumulated within the defined geometry, while this effect leads to splitting of the wall for the thicker T-in-T(prec) tube.

4. Conclusions

In the present manuscript, we confirm the concept that anodizing Ti in an organic electrolyte leads to nanotubular structures composed of an inner (low-quality and C-enriched) and an outer (high-quality and TiO_x-based) oxide shell. An optimized chemical treatment in piranha solution leads to the dissolution of the C-rich inner shell with the consequent formation of a single-walled nanotube morphology.

We also show that for anodization performed at relatively low temperature (10 °C), followed by annealing under most optimized conditions for tubes (*i.e.*, 450 °C in air), an additional feature is achieved, that is, the appearance of an extra inner tubular layer.

A detailed characterization of the three different tube types, namely DW, SW and T-in-T, shows that the new morphology (that appears only after annealing) exhibits features as double-walled nanotubes and, in particular, the formation of a carbon-rich inner shell (due to electrolyte species uptake). This is confirmed by the element distribution in the tube walls determined by EDX, AES measurements, and by TEM elemental mappings.

TGA and DSC characterizations show that DW and T-in-T have also similar T-dependent response that differs from that of SW nanotubes: specifically, carbon remnants in double-walled and tube-in-tube layers were shown to retard the crystallization process of tubes.

The main difference between a DW tube and the T-in-T(prec) is the width of the inner carbon rich shell. *I.e.*, low anodizing T establishes a reduced ion mobility and solubility that lead to the observed thickening of IS. Annealing causes incorporated C-species to be burned off as CO_2 and, as a consequence, generates mechanical stress. For the thicker wall in T-in-T(prec) this leads to the detachment of the inner shell from the outer shell and results in the formation of (smaller) nanotubes in the (larger) nanotubes. This peculiar tube configuration, with three distinct structure domains (namely, the internal and external tube walls, together with the void area between the inner and the outer tube) features additional advantages for applications where a large number of available surface sites is desired.

Acknowledgements

The authors would like to acknowledge ERC, DFG and the DFG Cluster of Excellence "Engineering of Advanced Materials" (EAM) for financial support.

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