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High aspect ratio TiO_2 nanotube layers obtained in a very short anodization time

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ABSTRACT

Over the past years, the growth of high aspect ratio (HAR) anodic TiO_2 nanotubes in a very short time (minute scale) has remained challenging. In the present report, TiO_2 nanotube (TNT) layers with HAR ≈ 450 were obtained during only 15 min of optimized anodization. The key feature is the use of NH_4F/H_2O/ethylene glycol (EG) electrolytes with the addition of lactic acid (LA) that prevents the dielectric breakdown and enables anodization at higher potentials compared to the classical NH_4F/H_2O/EG electrolyte without LA. The thickness and average diameter of the obtained TNT layers for 15 minutes' anodization at 160 V were approximately 80 µm and 170 nm, respectively. Furthermore, we show for the first time that high temperature anodizing, previously introduced as a driving force for the growth of HAR nanotubes in a short time, can be avoided by an accurate optimization of the anodization conditions at room temperature. The results clearly show that electrolytes containing LA can serve as a promising candidate for the ergonomic and economic production of HAR TNT layers on Ti substrates in very short anodization times, i.e. with the addition of LA, the anodization time can be significantly reduced from several hours or several days to 15–30 min.

1. Introduction

Self-organized anodic TiO_2 nanotube (TNT) layers, prepared by anodic oxidation of titanium [1,2], have attracted significant interest due to their intriguing properties for numerous applications such as H_2 production [3], photocatalysis [4], solar cells [5], or drug delivery [6]. One of the uniqueness of the anodic TNT layers is their customizable tube diameter and layer thickness to cater to the demand of different devices. TNT layers with thicknesses in the range of a few µm to approx. 30 µm attached to the underlying Ti metallic substrate are most typically used in the aforementioned applications [2–6]. To boost the performance of various nanotube-based devices, higher thicknesses, such as 50–300 µm are desired, which represent so-called high aspect ratio (HAR) TNT layers [7–12]. Within this range of layer thickness, a stand-alone TNT membrane, i.e. stable, functional, wholly delaminated TNT layer from the Ti substrate, and eventually a flow-through membrane, i.e. TNT layer with both ends opened, can be achieved [12].

Anodic TNT layers are most widely synthesized by the anodization of Ti foils in optimized organic electrolytes, comprised of ethylene glycol (EG) and small amounts of H_2O and NH_4F or HF, known as the "third generation of electrolytes" in the anodization field [7,8,13–17]. To achieve high aspect ratio structures, anodizations need to be carried out under relatively high constant potential or constant current, employing very long anodization times, i.e. several hours or up to several days [14–21]. However, these processes have poor economic figures due to extensive electrolyte aging, long duration, and high consumption of energy. As such, many efforts were devoted to accelerate the growth of HAR TNT layers based on the modification of EG-based electrolyte. Shankar et al. increased the size of cations of the fluoride-bearing species, instead of NH_4F, ~94 µm thick TNT layers were achieved within 48 h by Bu_4NF with higher ionic mobility [18], resulting in a growth rate of 0.032 µm/min. The presence of active F^- ions in the electrolyte is crucial for the continuous growth of TNT layers. Several works then attempted to maintain the excess F^- ions or to recycle the F^- ions in the electrolyte, by controlling the electrolyte at neutral pH [22] and the use of ethylenediaminetetraacetic acid (EDTA) as

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a chelating agent [19]. A more direct approach was by introducing H_2O_2 in the electrolyte to increase the oxidation rate to promote the nanotube growth [20]. However, the oxidizing power of H_2O_2 is available for only a certain period. These separate works have resulted in the highest growth rate of 2.25 μm/min [20] but attained the highest TNT layers thickness of 41.1 μm within 60 min [19] due to the non-linear growth rate, which were categorized as fast-growth TNT layers about a decade ago.

Despite considerable TNT layer thicknesses were achieved, no follow-up papers on these works were reported. Apparently, there is a great challenge to achieve long and extremely robust HAR TNT layers in a short time. The in-depth studies on the anodic growth mechanism of TNT layers in the past contributed to the fundamental understanding that the key to unlock high growth rates is to increase the anodization potentials without reaching the dielectric breakdown limits of the electrolyte [23]. The local breakdown is associated with very high local current densities on the anodized Ti and a significant increase in the local temperature [24,25]. Besides, the local breakdown is an autocatalytic and hence irreversible reaction. Once the breakdown is triggered, the high current density results in an increase in electrolyte temperature, which in turn, further increases the current density and then the electrolyte temperature, so the breakdown gets even more pronounced. Therefore, it is necessary to select the optimal anodizing conditions, which do not lead to dielectric breakdown.

So et al. were the first to report that the addition of lactic acid (LA) to the widely used NH_4F/H_2O/EG electrolyte allows the application of higher anodization potentials (120–150 V) without inducing electrical breakdown [9]. They have received a maximum TNT layer thickness of 148 μm in an hour of anodization at 60 ℃. However, as of other works on increasing the growth rate of TNT layers mentioned above, there was not any follow up work, especially targeting anodizations that could be carried out at room temperature to achieve ergonomic and economic production of HAR TNT layers.

Therefore, in this work, we revisit this topic and deeper evaluate the growth of HAR TNT layers in LA-containing electrolyte to investigate the breakdown limits and develop a sustainable protocol for the fast growth of HAR TNT layers. We demonstrate that the use of EG-based electrolyte containing LA with optimized electrolyte age is the key parameter that enables the use of high potentials for high nanotube growth rate, yielding HAR TNT layers in a comparably shorter time than reported in the literature. In other words, for the first time, we suggest a protocol to achieve fast growth rates of TNT layers without any tedious conditions behind (such as heating, cooling, etc.) which is one of the challenges that are still to be beaten for anodic TNT layers to become industrially viable and exploitable. Moreover, we examined the surface morphology and dielectric breakdown potentials of the HAR TNT layers grown using different anodizing potentials, anodizing times, and LA-containing and LA-free electrolytes. In comparison to the existing literature on LA-containing electrolytes, all anodizations were carried out at room temperature.

2. Experimental

Titanium foils (0.127 mm thick, 99.7% purity, Sigma-Aldrich) were cleaned via ultra-sonication with isopropanol and acetone sequentially, then rinsed with isopropanol and dried at room temperature. Anodization was performed in a two-electrode cell with platinum and titanium foils as counter and working electrodes, respectively. The Ti foil was pressed against an O-ring of the electrochemical cell with an area of 1 cm^2 opened to the electrolyte. All the chemicals and materials involved in these experiments were of analytical grade, without any further purification. A high voltage potentiostat-galvanostat (PGU-200 V, IPS Elektroniklabor GmbH) was used. For all anodizations, the applied potentials were continuously increased at the rate of 1 V/s from the open-circuit potential (OCP) to fixed potentials (60–160 V) and then held constant until the end of the process [26]. EG-based electrolytes were used for the anodization of Ti foils, containing 0.176 M NH_4F and 1.5 vol% H_2O [27] with or without the addition of 1 M LA. The concentration of 1 M LA was selected after preliminary experiments from different concentrations of LA: 0.01, 0.1 M, and 1 M (experiments not shown). The anodization times (15, 30, 60, 90, and 120 min) were varied to investigate the growth of nanotubes and observe the initial breakdown occurrence.

The double step anodization was also employed in this work to increase the homogeneity of the resulting nanotubular surfaces. For this purpose, the Ti foils were first anodized in an EG-based electrolyte containing LA at 100 V for 15 or 60 min, and then the grown TNT layer was removed by ultra-sonication in deionized water. The resulting pre-patterned Ti foils [28] were used for the second anodization, which was performed in the same electrolyte as for the first anodization, using an anodization time of 15 min.

To investigate the morphology of the obtained TNT layers, a high-resolution field emission scanning electron microscope (FE-SEM, FEI Verios 460 L) at 50 pA of scanning current and 5 kV of accelerating voltage was employed to image the TNT layers. The inner diameter of the TNTs and the thickness of the TNT layers were measured from the SEM images taken on the surface and cross-sectional views. The measured values were statistically evaluated using at least 100 values for the diameters and at least 10 values for thicknesses, respectively.

3. Results and discussion

In the first step, it was necessary to find the optimal electrolyte age to use elevated anodizing potentials in the subsequent anodization without breakdown events.

It is known from the literature [29] that initial aging of the electrolyte is required to receive homogeneous TNT layers. Furthermore, with repetitive use of the electrolyte and thus increase of the electrolyte age the nanotube diameter increases while the TNT layer thickness decreases due to a gradual change of electrolyte composition stemming from the electrolyte reactions (i.e. decrease in fluoride ions and increase in H_2O content) resulting in lower aspect ratios of the TNT layers [29].

3.1. Optimization of electrolyte age

In this work, no initial aging of the electrolyte was carried out. Instead, electrolytes of different age, between 0 and 50 h aging time, were used at potentials of 80 and 100 V for 15 min to find the optimal electrolyte age. Fig. 1a shows the effect of electrolyte age on the TNT layer thickness obtained in electrolytes consisting of EG/0.176 M NH_4F/1.5 vol% H_2O with and without 1 M LA, with two different applied potentials at 80 and 100 V. The result shows that in both electrolytes with and without LA, the fluoride concentration remained high enough to support the TNT layer growth within up to 50 h of electrolyte age. Even though the fresh electrolytes had nominally the highest fluoride content, only moderate TNT layer thicknesses (~5–10 μm) could be obtained, and the layers as such were easily lifted off from the Ti substrate. This is most likely connected to the high fluoride concentration in completely fresh electrolytes without aging, resulting in an extremely high etching rate. This confirms the rule of thumb that the initial aging of electrolytes for ~9 to 15 h is necessary to prepare TNT layers with appropriate quality [29]. With the increasing electrolyte age from 5 to 22 h, in the moderate age period, the TNT layer thicknesses increased in both electrolytes, compared to fresh electrolytes. As expected, the nanotube layers prepared at 80 V were considerably thinner than those prepared at 100 V [30,31].

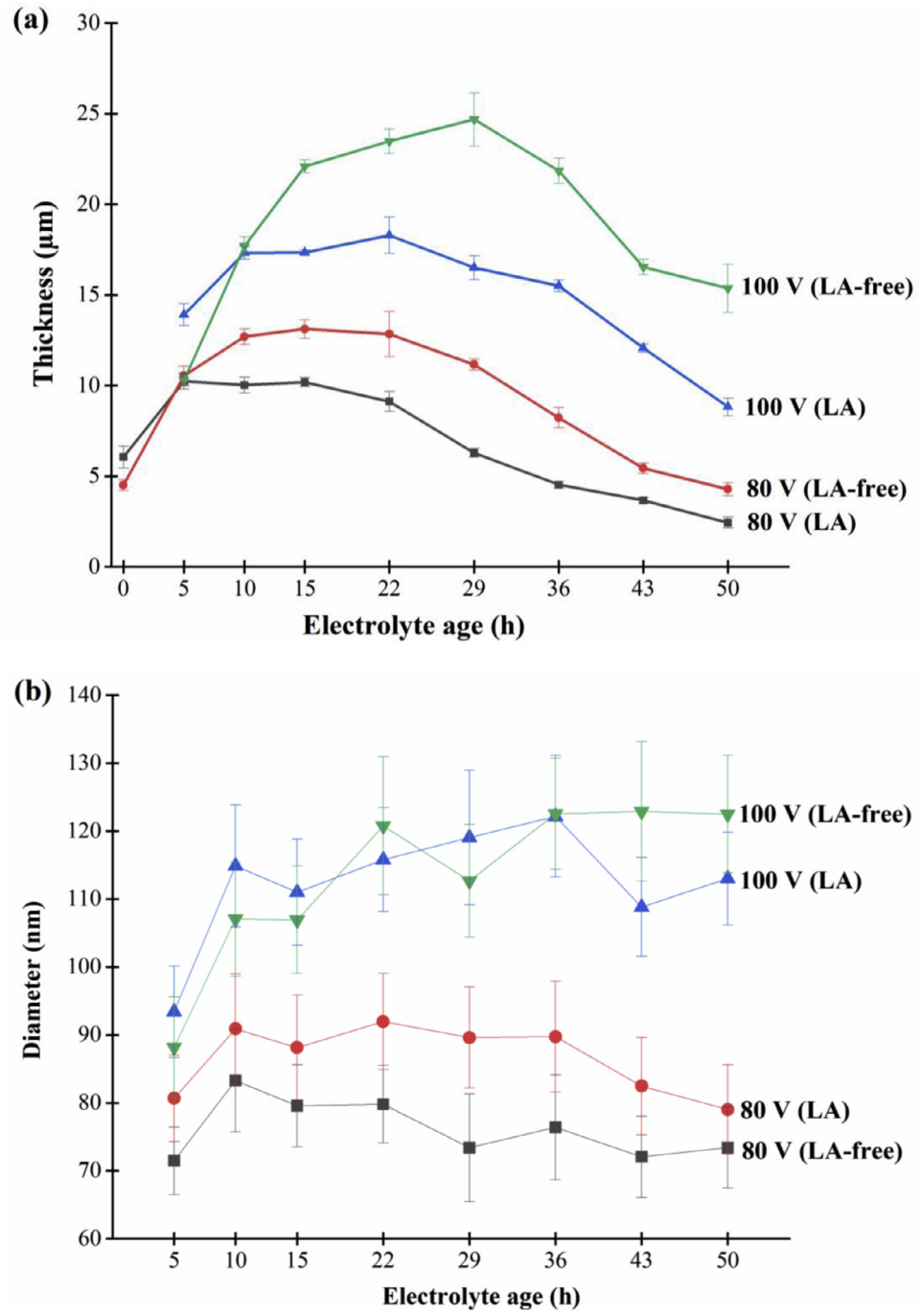

Fig. 1. (a) Thicknesses and (b) inner diameters of TNT layers anodized in LA-containing and LA-free electrolyte between 0 and 50 h of aging time at 80 and 100 V for 15 min.

Depending on applied potentials, the time of 22 h for aging was selected as the best aging time to prevent the breakdown during the main anodization runs at potentials above 100 V and at the same time to achieve the thickest layers. As seen in Fig. 1, with increasing aging time from 0 to ~10–15 h, the nanotube layer thicknesses increased for both LA-containing and LA-free electrolyte at 80 and 100 V, whereas after 29 h the nanotube layer thickness begun to decrease. Besides, with aging times shorter than 22 h, the electrolytes were still prone to breakdown at elevated potentials. In electrolytes older than ~29 h, also at elevated potentials, the nanotube layers were thinner than in electrolytes of 22 h age. Thus, the aging time of 22 h was chosen as the most favorable time. However, the deviations of TNT layer thicknesses for each electrolyte in this moderate age period were relatively small, as demonstrated by error bars in Fig. 1, which confirm that the electrolytes can be re-used in this age range without a huge quality loss of the TNT layers.

The dependence of the TNT diameters on the electrolyte age is shown in Fig. 1b. A gradual increase of the diameters for the TNT layers anodized at 100 V with increasing electrolyte age can be seen, while for anodization at 80 V, no clear dependency of the TNT diameter on the electrolyte age was observed. For different electrolyte ages between 5 and 50 h, the average nanotube diameter was in the range of 90 to 120 nm for anodization at 100 V and in the range of 75 to 90 nm for anodization at 80 V. The higher anodization potential is related to the high electric field, which ex-

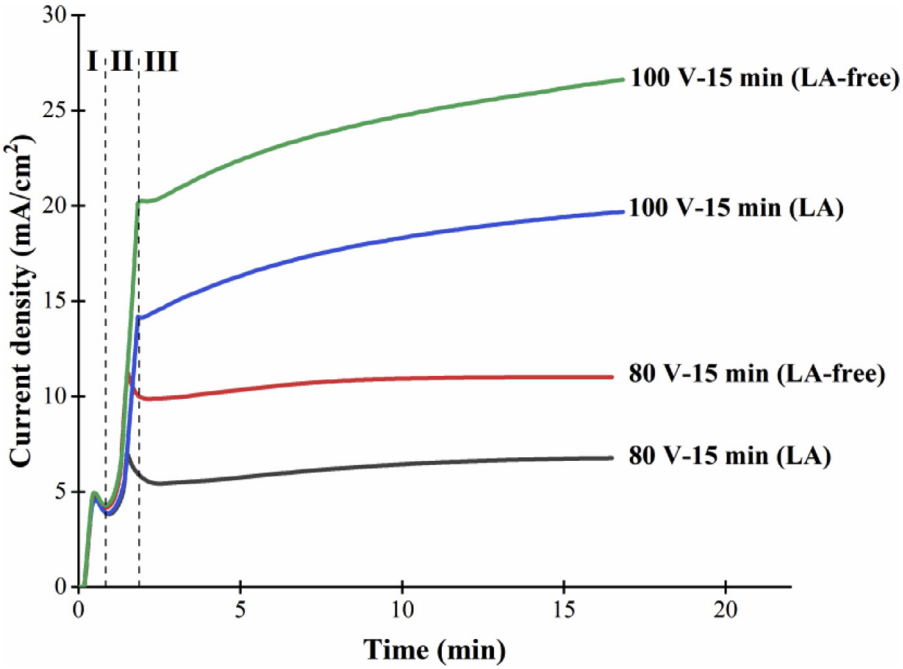

Fig. 2. Current-density vs. time curves of TNT layers anodized in LA-containing electrolyte and LA-free electrolyte at 80 and 100 V for 15 min in their respective 22 h aging time. The dashed lines indicate three different stages of the TNT layer growth.

cavates larger pits on the Ti surface during the initial anodization process and over time produces TNTs with large average diameter [1].

Based on the results presented in Fig. 1a, b, an electrolyte age of 22 h was selected as the optimal age for the following experiments as it leads to a high TNT layer thickness without the risk of dielectric breakdown for both types of electrolytes.

3.2. The effect of LA-containing and LA-free electrolytes on current density vs. time curves

Fig. 2 shows the current density–time transients recorded during the TNT layer growth in electrolytes with and without LA at 80 and 100 V for 15 min. It can be seen that all curves show the three typical stages of anodization: (I) formation of a barrier oxide, (II) surface activation and pore growth, (III) self-ordering TNT layers under steady state conditions, as known from the literature [1,32,33]. The anodizing current density at the beginning of anodization (stage I) in the LA-containing electrolyte (9.8 mA/cm^2 at 80 V and 18.9 mA/cm^2 at 100 V) was lower than in their respective LA-free electrolyte (13.3 mA/cm^2 at 80 V and 24.6 mA/cm^2 at 100 V). Note that all anodizations carried out in LA-containing electrolyte showed generally lower current-densities than the anodizations carried out in LA-free electrolytes under the same conditions. This is in good agreement with the literature [9]. In fact, it was analyzed by X-ray photoelectron spectroscopy that LA is adsorbed on the TiO_2 surface to retard the active dissolution of Ti^{4+} and shift the breakdown potential towards higher potentials [9]. Thus, lower current densities were recorded in LA-containing electrolytes. The effect of LA addition was much more evident for the anodizations at the higher potential (100 V).

3.3. Effect of anodization time and potentials on the surface morphology of the TNTs

Figs. 3 and 4 compare typical SEM top views of TNT layers obtained in LA- containing and LA-free electrolytes (22 h of age), respectively, under different anodization potentials and times. As one can see, TiO_2 nanotubes have been formed under these anodization potentials in both electrolytes. As discussed for the current-densities results (Fig. 2), the current-densities were higher for the anodization in LA-free electrolyte, the electrolyte was consequently heated to a higher temperature, which leads to the breakdown in LA-free electrolyte at lower potentials (at 100 V before 60 min) compared to the LA-containing electrolyte (without breakdown at 100 V up to 120 min and at 140 and 160 V for 15 min each). In other words, the anodization in LA-free electrolyte at e.g. 160 V accelerates the occurrence of breakdown and disrupts the TNTs growth. Moreover, the morphology of the TNT layers synthesized in both electrolytes at lower potentials (60–100 V) and at the shortest time (15 min) is not well pronounced and homogenous. There are apparent traces of the remnant porous TiO_2 layer from the early stages of anodization [1]. However, with increasing anodization times and potentials, the presence of these porous layers is strongly reduced and a well-defined nanotubular structure appears.

3.4. Effect of anodization time and potentials on the thickness and diameter of the TNTs

Regardless of the exact composition of the electrolyte, anodization potentials and times are important factors to control the TNT diameter and thickness of the TNT layers. It is mainly the applied potential that determines the electric field strength across the growing oxide layers, therefore affecting the migration of ions, but of course, the conductivity and chemistry of electrolytes have some influence as well [1, 34].

The present results show that anodization in the LA-free electrolyte at the lower potentials (80 and 100 V) leads to thicker TNT layers compared to LA-containing electrolyte. However, a completely different situation is observed at higher potentials ($\geq$ 120 V), in particular, for extensive anodization times, where the anodization in LA-free electrolyte is simply impossible. This is because of the significant and fast increase in the electrolyte temperature, which leads to breakdown event.

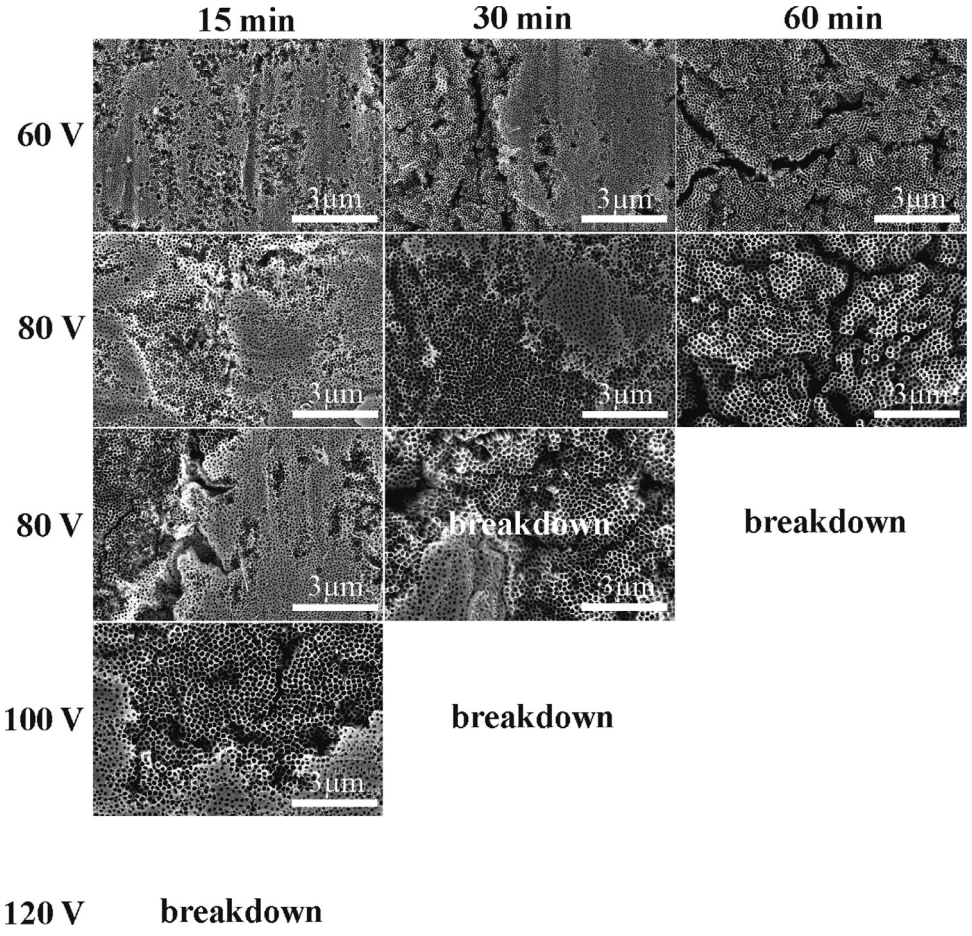

Fig. 3. SEM top-view images of TNT layers anodized in LA-free electrolyte at different times and potentials in electrolytes with 22 h of aging time.

On the other hand, the LA-containing electrolyte is advantageous for higher anodization potentials. For example, 160 V can be applied for a short time without breakdown event. These results elucidate the importance of the addition of LA to the EG-based electrolytes against the breakdown events. As explained above, LA can shift the breakdown potential towards the higher potentials [9]. However, it is the balance of anodization potential and time that is the key to the control of anodic TNT layer growth behavior. It can be seen that with increasing anodization potential and time, the thickness of the TNT layers increased persistently (Fig. 5a). However, this increase is more noticeable for the anodization in LA-free electrolyte due to a sudden increase in the temperature, which leads to breakdown at comparably lower anodization potentials. In contrast, the anodization in LA-containing electrolyte can lead to a comparably higher thickness within shorter anodization times with the prevention of the breakdown. Overall, our results clearly corroborate findings reported by So et al. [9].

Fig. 5a provides an overview of TNT layer thicknesses obtained after anodization in both types of electrolytes at different potentials for different anodization times. As one can see, the slope of the curves, which translates to the growth rate, increases with the increase of applied potential. In a comparison of layer thicknesses, it is apparent that in LA-free electrolyte, a thickness of ~89 μm was achieved after 60 min at 100 V. However, with a breakdown in the final stage of the experiment, which the TNT layer lifted off from the Ti substrate during subsequent sonication. In contrast, in the LA-containing electrolyte, TNT layers with a thickness of ~80 μm can be obtained already after 15 mins anodization at 160 V. Also, a thickness of ~82 μm was achieved after 30 mins at 140 V, without any breakdown or delamination issues.

According to Fig. 5b, the average nanotube diameter was found to be in the range of 80 to 175 nm in LA-containing electrolyte and in the range of 90 to 155 nm in the LA-free electrolyte at 80 V. It can be seen that variation in diameter is more affected by the anodization potential and time rather than by the composition of the electrolyte.

The largest TNT diameter of ~210 nm was achieved in LA-containing electrolytes at an anodization potential of 100 V applied for 120 min, and at 120 V and 140 V for each 30 min anodization. Based on previous reports that the anodization potential has a significant impact on the growth rate [17,35], with the LA-containing electrolyte, at the high potential, we developed HAR TNT layers (aspect ratio, ~450) in short time anodization for 15 min at room temperature.

Table 1. summarizes the notable studies in the literature on the rapid growth of anodic TNT layers with their anodization conditions. It can be seen that a very high growth rate of TNT layers in a very short time was achieved in this work compared to previous reports. In fact, the highest growth rate was achieved in this work for processes without any further additional heating of the electrolyte (e.g. to 60 °C as in Ref. [9]).

Among these studies, certainly So et al. [9] has documented the most remarkable growth rate for anodic TNT layers by the aid of LA in the electrolyte at elevated temperature (60 °C). An ~18 μm thickness was achieved within 1 min (equivalent to ~18.2 μm/min), and ~148 μm within 1 h (equivalent to ~2.5 μm/min) by the anodizations at 60 °C. Their results clearly show that the extremely high

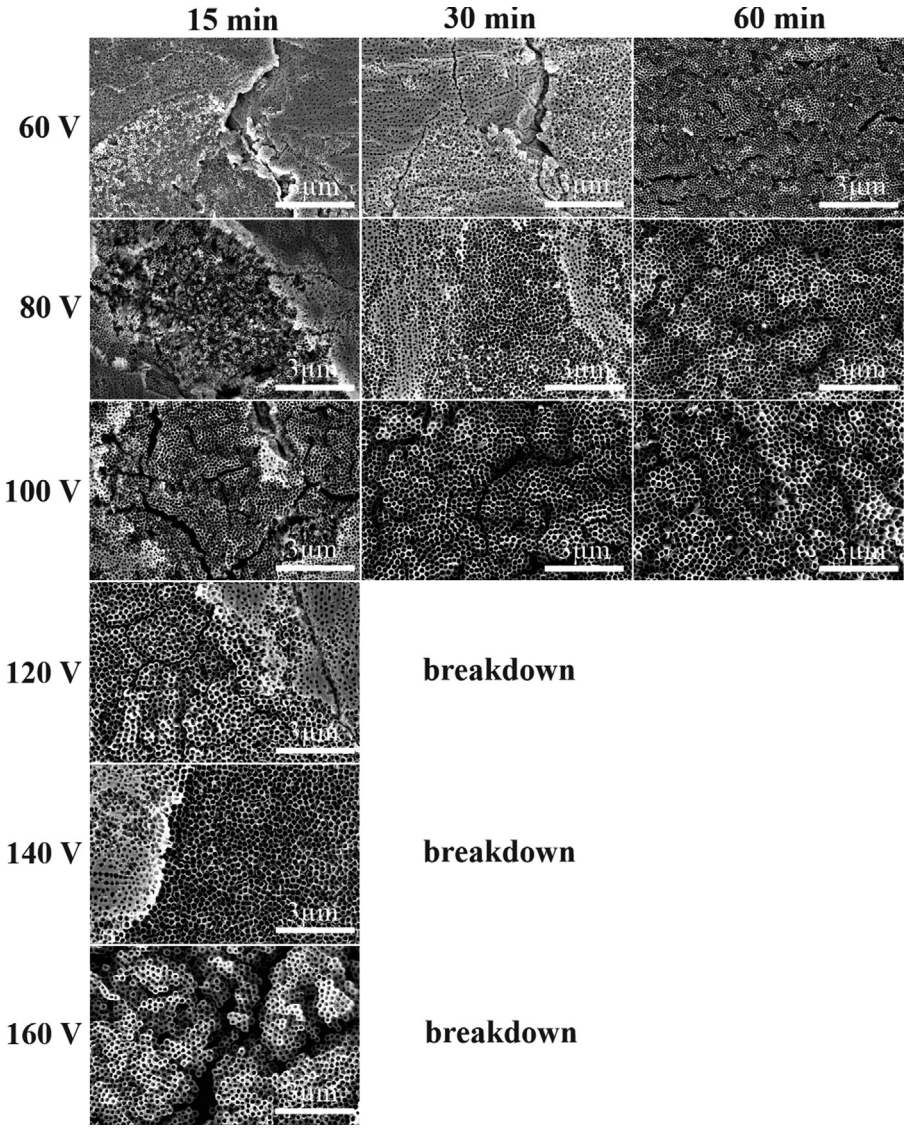

Fig. 4. SEM top-view images of TNT layers anodized in LA-containing electrolyte at different times and potentials in electrolytes with 22 h of aging time.

growth rate is only possible to achieve at the beginning of the anodization process, and the growth rate decays exponentially over time. Despite the reason is unknown, their procedure is mainly efficient for growing thinner TNT layers (~20 μm). In contrast, we achieved a high thickness of ~80 μm within 15 min (equivalent to ~5.3 μm/min) by carrying out the anodization at the room temperature, which requires a less tedious set-up and is cheaper than handling electrolytes at elevated temperature. Altogether, we developed a more sustainable anodization procedure for the growth of HAR TNT layers, with a balance between efficient growth and reasonable energy consumption.

3.5. Effect of double-step anodization on the surface of TNT layers

With the tailored procedure to achieve high thickness TNT layers within a short period, it is also essential to achieve a homogeneous TNT surface for functional applications. In order to obtain TNT layers without any traces of the initial porous TiO_2 layer with the highest possible degree of self-organization, the double step anodization protocol was adopted subsequently [28]. In this process, a sacrificial amount of Ti was anodized first, afterwards, the as-formed TNT layer was removed and the pre-patterned Ti substrate was submitted to a second anodization process. Both anodization steps were carried out under identical conditions in LA-containing electrolyte. The advantage is that most of the initial porous layer is lost due to the first sacrificial anodization.

Fig. 6 shows the SEM images of TNT layers after the first and the double-step anodization at different anodization times, i.e. 15 and 60 min. It can be seen that the double step anodization has yielded more organized TNTs without the initial porous oxide layers. The observation is aligned with the literature that double- [28,39] or multi-step [40,41] of repetitive anodization gradually improves the ordering and homogeneity of the TNT layers [38–40]. The removal of sacrificial TNT layer to create the pre-patterning effect is only effective with a substantial TNT layer thickness [28], which is perceived as a time and energy consuming step. Therefore, the accelerated growth of TNT layer by the addition of LA in NH_4F/H_2O/EG-based electrolyte presented here effectively facilitates the multi-step anodization process.

4. Conclusion

This research shows the successful anodization of Ti foil towards HAR TNT layers by using NH_4F/H_2O/ethylene glycol elec-

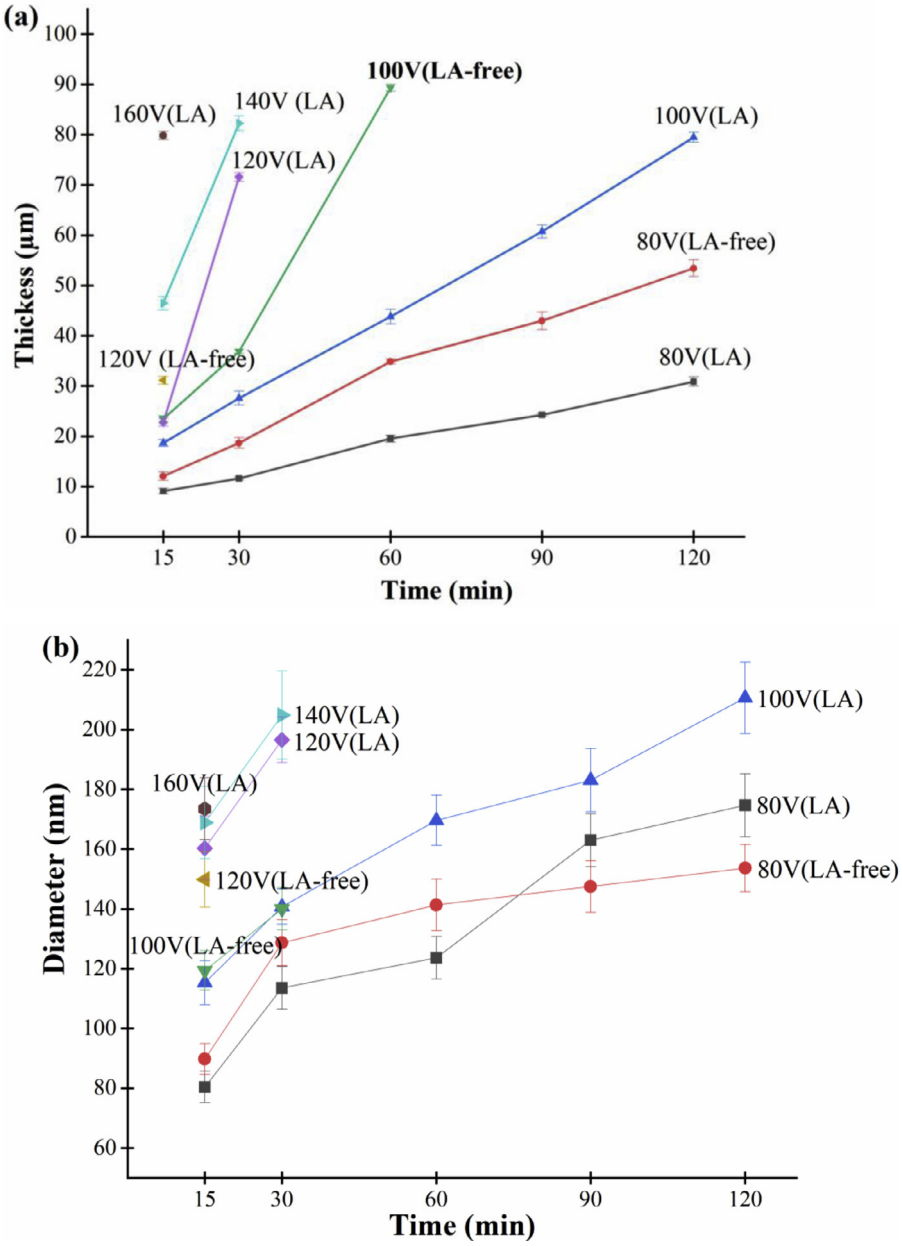

Fig. 5. (a) Thicknesses and (b) inner diameters of TNT layers anodized in LA-containing electrolyte and LA-free electrolyte (both with 22 h of aging time) at 80, 100, 120,140, and 160 V for different anodization times. The bold labelled TNT layer in (a) lifted off from the Ti substrate after 60 min anodization.

Table 1
Different anodization conditions used for fast-growing HAR TNT layers.

Electrolyte composition	Potential (V)	Time (min)	Thickness (μm)	Growth-rate (μm/min)	Ref
0.3 wt% NH_4F- 0.13 wt% H_2O- EG	60	1080	18.5	0.017	[22]
0.3 wt% NH_4F- 0.13 wt% H_2O- EG	60	120	23	0.191	[36]
0.3 wt% NH_4F- 0.13 wt% H_2O- EG	60	1020	220	0.215	[8]
0.25 M $Na_2(H_2EDTA)$- 5 M NH_4F-5 vol% H_2O- EG	80	60	41.1	0.685	[19]
1.5 M LA- 0.1 M NH_4F- 5 wt% H_2O- EG	120	10	7	0.700	[37]
1.5 M LA- 0.1 M NH_4F- 5 wt% H_2O- EG	120	10	25.0	1.504	[9]
1.5 M LA- 0.1 M NH_4F- 5 wt% H_2O- EG	120	8.3	16	1.927	[38]*
5 wt% H_2O_2–5 wt% NH_4F- EG	60	1	2.2	2.250	[20]
1.5 M LA- 0.1 M NH_4F- 5 wt% H_2O- EG	120	60	148	2.466	[9]*
1.5 M LA- 0.1 M NH_4F- 5 wt% H_2O- EG	120	10	73.8	7.385	[9]*
1.5 M LA- 0.1 M NH_4F- 5 wt% H_2O- EG	150	0.3	4.8	16.000	[9]*
1.5 M LA- 0.1 M NH_4F- 5 wt% H_2O- EG	150	1	18.2	18.200	[9]*
1.5 M LA- 0.1 M NH_4F- 5 wt% H_2O- EG	150	0.6	14.3	23.833	[9]*
1 M LA- 0.1 M NH_4F- 1.5 wt% H_2O- EG	160	15	79	5.266	Present work

* In this report the anodization was carried out at 60 ℃.

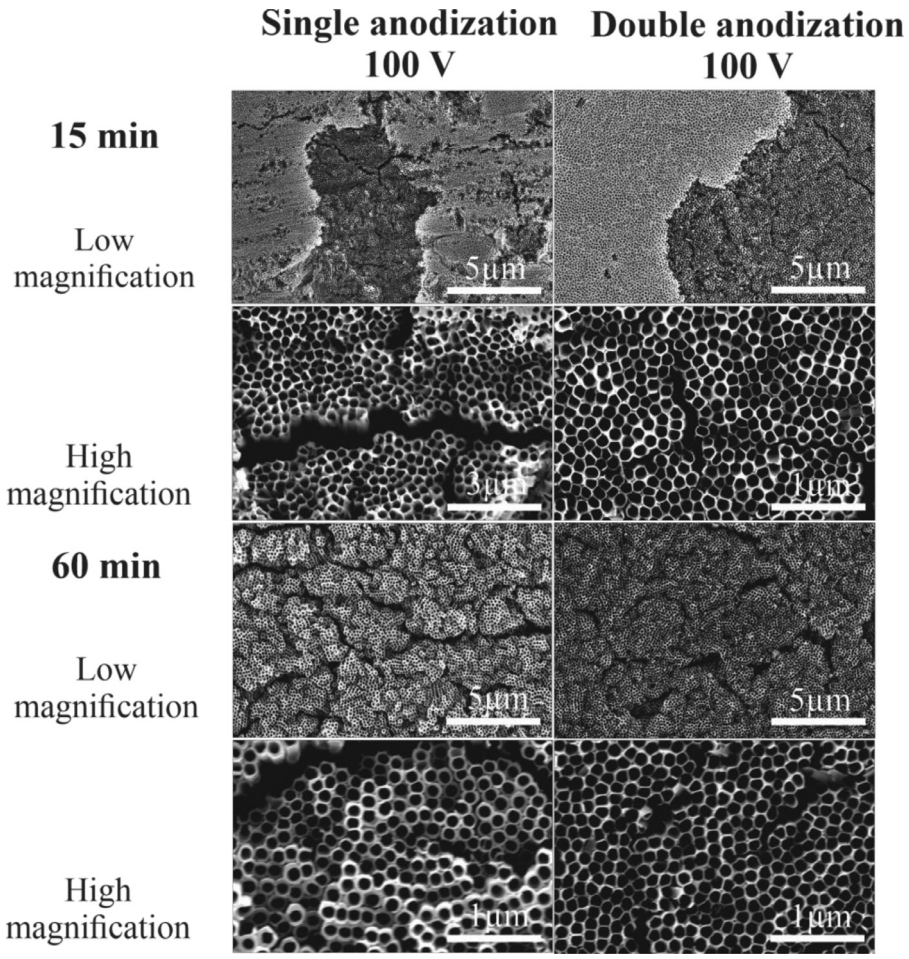

Fig. 6. SEM top-view images of TNT layers anodized (single and double anodization) in LA-containing electrolyte at 100 V for 15 and 60 min.

trolyte with the addition of LA at very high potentials and room temperature without dielectric breakdown. The results clearly show that controlled electrolyte age and application of high potentials, HAR (~450) TNT layers can be obtained within very short anodization times. The anodization time can be reduced from several hours without LA addition to 15–30 min due to the possibility of the application of very high anodization potentials. This approach shows a promising pathway without any additional process such as heating or cooling the electrolyte, etc., to obtain robust TNT layers without dielectric breakdown in a very short time at the room temperature and in an ergonomical and economical way.

Credit author statement

HS and JMM designed experiments; MA – synthesis of nanotubes by anodization, SEM characterizations; HS and SN supervised the synthesis and experiments, MA, HS and JMM wrote the manuscript and carried out revisions; all others reviewed and edited the manuscript; JMM supervised the whole team and provided support. All authors have read and agreed the published version of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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