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# Understanding the Influence of Electrolyte Aging in Electrochemical Anodization of Titanium

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**Keywords:** anodization, titanium, titania nanotubes, titania nanopores, electrolyte aging

## Abstract

Titania nanotubes or nanopores self-ordered on electrochemically anodized (EA) titanium have been widely applied towards photocatalysis, solar cells, purification and biomedical implants. As a result, significant research has been focused towards optimizing its fabrication to enable controlled, stable and reproducible nanostructures. Among these, the use of organic-based electrolyte, like ethylene glycol (with $NH_4F$ and water), to anodize Ti has been widely applied and researched. Interestingly, among the various influencing EA factors, electrolyte aging (repeated EA using non-target Ti, prior to EA of target Ti substrate) has been underexplored, with only few studies aiming to optimize electrolyte aging and its influence on the nanostructure yield. Moreover, many research laboratories utilize electrolyte aging in Ti anodization, but this practice is seldom reported. In this extensive and pioneering review, we discuss and detail electrolyte aging with respect to Ti anodization to fabricate controlled nanostructures, and its influence on nanostructure characteristics including morphology, chemistry, stability and application-specific performance (photocatalysis and bioactivity) of the anodic titanium oxide. This review will inform future research aimed at optimizing electrolyte aging and Ti anodization to fabricate controlled nanostructures catering to specific application needs.

## 1. Introduction

Electrochemical anodization (EA) is one of the cost-effective and scalable technologies to nano-engineer titanium to fabricate controlled nanotopographies, such as titania ($TiO_2$) nanotubes (TNTs) and nanopores (TNPs) [1]. The ease of control over the characteristics of $TiO_2$ nanostructures by EA has enabled their application in a wide range of industries, including purification, biosensing, solar cells, and biomedical implants [2-4]. Further, $TiO_2$ nanotubes (TNTs) are the most researched Ti nanostructure in terms of optimization of both the fabrication and the application-specific performance. Interestingly, the concept of repeated anodization of non-target Ti in freshly prepared electrolyte towards 'aging' or 'conditioning' of the electrolyte (prior to anodizing target Ti) is frequently used in EA of Ti and its alloys but remains poorly specified or researched. Aging has been reported for electrolytes made in organic solvents including ethylene glycol, dimethyl sulfoxide (DMSO), and glycerol (**Table 1**). So far, it is accepted in the literature that the use of aged electrolytes allows for improved ordering and stability of the nanotubes. However, this phenomenon has not been widely documented. **Table 1** summarizes the key studies focussed on electrolyte aging in Ti EA, and its influence on the resultant TNTs and TNPs. Note that electrolyte aging has also been used to fabricate highly ordered alumina nanostructures by EA of Aluminium [5, 6]. Further, anodized Zirconium has been aged via immersion in the anodization electrolyte or in water, which led to a transformation from a nanoporous to a nanotubular morphology [7]. The current paper focusses on aging of the electrolyte (rather than aging of the nanostructures) to anodize Ti to fabricate $TiO_2$ nanostructures.

Overall, Ti anodization electrolyte aging is governed by the following rules:

1. EA performed on non-target Ti substrate at a specific voltage and time
2. Generally defined by the length (time) of anodization performed
3. Ti used for electrolyte aging is discarded and fresh target Ti is used as anode, once the aging is complete. It is accepted that the EA of target Ti with aged electrolyte will yield improved ordering of anodic $TiO_2$ nanostructures with enhanced stability and interfacial strength of anodic film to the underlying substrate [8] [9].
4. The electrochemical cell used, to great degree, defines the electrolyte conditioning upon aging. Hygroscopic electrolytes containing ethylene glycol can absorb water with time (increasing conductivity), when EA is performed in unshielded electrochemical cells [10, 11]. However, when EA aging is performed in enclosed cells, water is continuously consumed (not absorbed) from the electrolyte, thereby reducing conductivity [8, 12]. It is

interesting that many aging studies do not specify if the electrochemical cell was shielded or open, an important criterion which defines the electrolyte aging.

5. Most Ti EA studies reporting fabrication of nanotubes or nanopores, practise electrolyte aging, however, it is not appropriately disclosed in literature.

**Figure 1** presents the basics of electrolyte aging and what changes in electrolyte and the nanostructures when same electrolyte is repetitively utilized [12]. Clearly, electrolyte aging and its influence is not appropriately researched or reviewed. Hence, in this pioneering attempt, we aim to understand electrolyte aging and its influence on the $TiO_2$ nanostructures fabricated using Ti anodization. The review informs the reader how and why the characteristics of the nanostructures change, and simplifies the concept of electrolyte aging, to enable further optimizations in Ti anodization, yielding controlled, reproducible, and stable nanostructures, matching specific application needs.

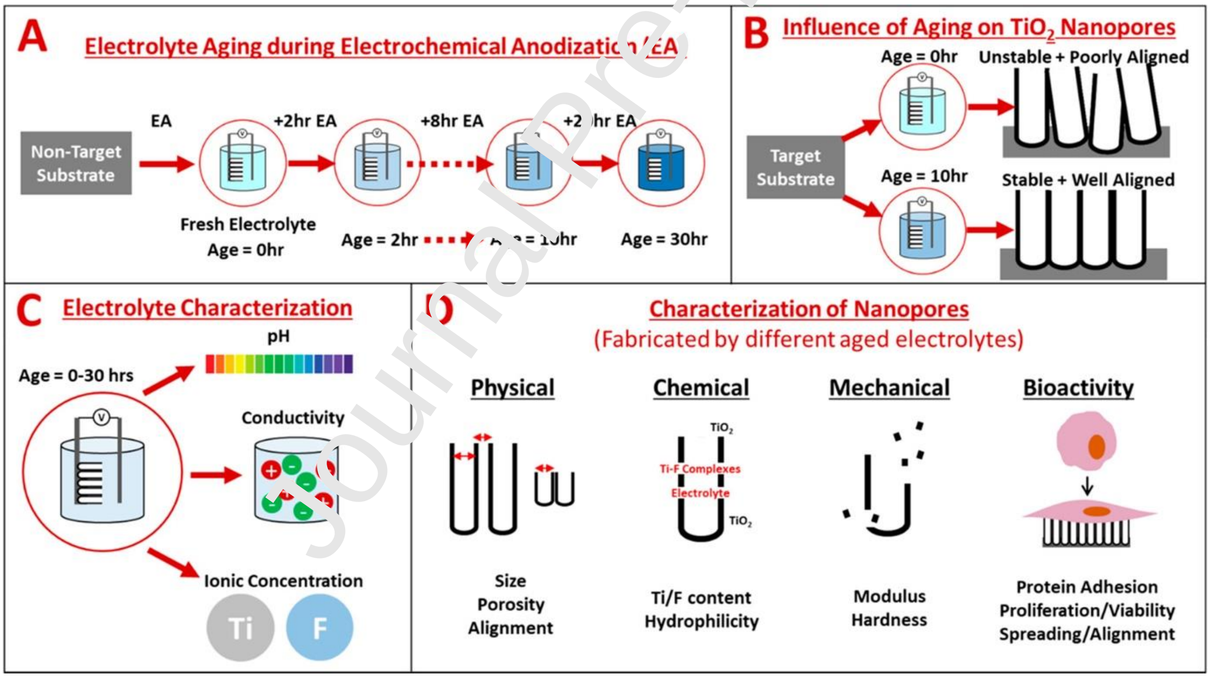


**Figure 1.** Influence of electrolyte aging on the characteristics of the anodized nanostructures for Ti anodization. Schematic representation of (A) electrolyte aging; (B) influence of aging on stability/alignment of nanopores; (C) changes in the electrolyte during aging; and (D) influence of aging on the topographical, chemical, mechanical and bioactivity characteristics of nanopores. Adapted with permission from [12].

**Table 1.** Summary of studies investigating electrolyte aging and its influence on the $TiO_2$ nanostructures fabricated using Ti anodization. EG: ethylene glycol; DMSO: dimethyl sulfoxide; EA: electrochemical anodization; TNTs: titania nanotubes; TNPs: titania nanopores; DSSC: dye-sensitised solar cells.

| **Author, Year** | **Nanostructure and substrate** | **Electrolyte Solvent** | **Aging** | **Outcome for EA with Aged Electrolyte** | **Ref** |
|---|---|---|---|---|---|
| Yoriya, 2007 | TNTs on Ti foil | DMSO | 40V, 70h | ▪ High electrolyte conductivity<br>▪ Shorter length TNTs with open pores | [11] |
| Lee, 2009 | TNTs on Ti foil | EG | Conductivities: 40 µS/cm and 80 µS/cm | ▪ Increased electrolyte conductivity with EA time (aging)<br>▪ Increased TNTs length<br>▪ Fibre-like structure observed for low conductivity (highly aged) electrolyte<br>▪ High cell efficiency and smaller charge-transfer resistance (for application as DSSC) | [10] |
| Zhu, 2011 | TNTs on Ti foil | EG | 58V, 17h | ▪ High conductivity and increased pH<br>▪ Increased TNTs length and widen wall thickness.<br>▪ Improved adhesion of TNTs with the Ti.<br>▪ Increased photoelectrochemical properties | [9] |
| Jarosz, 2014 | TNTs on polished Ti foil | Glycerol | 2h, varied voltages | ▪ Reduced pore diameter with time | [13] |
| Sopha, 2015 | TNTs on Ti foil | EG | 0, 6, 25, 50h at 60V | ▪ Conductivity increases with aging<br>▪ Low aspect ratio TNTs | [14] |

| | | | | | |
|---|---|---|---|---|---|
| Gulati, 2015 | TNTs on Ti wire | EG | 0, 5, 10, 20, 25, 30h at 75V | ▪ Conductivity reduces with aging<br>▪ Ti ion concentration increases<br>▪ Increased ordering and stability | [8] |
| Li, 2018 | TNPs on micro-machined Ti foil, wires and implants | EG | 75V, 10h | ▪ 1st step EA on rough and micro-machined Ti using fresh electrolyte can cause instabilities and cracks<br>▪ Increased hardness and Young’s modulus (for TNPs on Ti wires) | [15] |
| Gulati, 2018 | TNPs on micro-machined Ti discs | EG | 75V, 10h | ▪ Aged EA ‘conserves’ the underlying micro-roughness and superimposes nanotopography, while fresh EA ‘consumes’ the underlying features.<br>▪ Increased hardness and Young’s modulus | [16] |
| Suhadolnik, 2020 | TNTs on Ti foil | EG | 60V, 6h<br>(1-20 days, one EA each day) | ▪ Lower conductivity, increasing water content, reducing F<br>▪ Reduced TNTs length with aging<br>▪ Open pore TNTs for 5th and 13th day aged electrolyte<br>▪ Increased photocatalytic activity | [17] |
| Guo, 2021 | TNPs on micro-machined Ti foil | EG | 10h, 20h, 30h at 80V | ▪ Reduced conductivity and increased pH<br>▪ High Ti ions and low free F ions in electrolyte<br>▪ Improved ordering: 10-20h aged<br>▪ Increased hardness and | [12] |

| | |
|---|---|
| | Young’s modulus<br>▪ Increased hydrophilicity and favourable bioactivity |

## 2. Anodization of titanium and its alloys

Zwilling et al. are credited with the first report on Ti anodization in HF containing chromic acid electrolytes yielding self-ordered anodic oxide [18, 19]. Nanotubular layers of about 500nm thickness were fabricated that had sidewall inhomogeneity and were not well organized. Interestingly, 20 years prior to work by Zwilling et al., Kelly et al. reported porous titania oxide layer formation for low fluoride concentrations, however, the likely self-ordered TNTs were not imaged by electron microscopy [20] [1]. These landmark studies have driven further advances in Ti anodization research.

The wide range of applications for TNTs is attributed to the ability of the EA process to tailor the morphology of the nanotubes catering to the specific applications [21]. Although the self-ordered nanotubular/nanoporous morphology depends on numerous EA conditions (voltage, current, time, pH, temperature, etc.), electrolyte choice and composition has been widely optimized to fabricate highly ordered TNTs [1, 22]. For instance, if EA is performed in acidic aqueous solutions without $F^-$ ions, the $TiO_2$ film will be of a barrier type, whereas, the presence of F- ions in the electrolyte promotes the formation of self-organized TNT [1, 23, 24].

Depending on the F-containing electrolyte, four generations of TNTs with different morphologies (varied maximum thickness/length, ordering, and wall roughness) can be fabricated [25]. TNTs from the 1st generation are formed in aqueous solutions of hydrofluoric acid. Resultant TNTs are poorly ordered, with a maximum thickness of 0.5 µm [26]. Because of the dissolving power of HF, the 2nd generation utilized fluoride salts as $F^-$ source ($NH_4F$/NaF 0.1-0.5 wt. %) [27]. The morphology of these TNTs can be defined as ordered and slightly ribbed [28]. Currently, TNTs of 3rd or 4th generations are fabricated in organic solvents, mainly polyhydric alcohols (i.e., ethylene glycol or glycerol) based electrolytes with a small amount of water (0.1-5) wt.% and $NH_4F$/NaF salts (0.1-0.5) wt.% [29-31]. Further, recent advances include the use of monohydric alcohol as an electrolyte to anodize Ti, yielding colored anodic titanium oxide with nanotubular structures [32]. The introduction of organic components combined with F-based salts usually shows lesser dissolving power than those developed in water media. This allows the formation of well-ordered $TiO_2$ nanotubes or nanopores. Note that water addition favors the dissolution of F-based salts and, consequently, the $O^{2-}$ and $OH^-$ anions in organic media are formed [33, 34].

The growing mechanism of self-ordered TNTs is still controversial. According to the electrolyte composition and operating conditions, several growth mechanisms have been proposed to explain the TNTs formation in F-containing electrolytes. Traditional theories such as *field-assisted dissolution* and *field-assisted ejection* involve the formation of pore channels through titanium hexafluoride layer dissolution from top-down [35, 36]. Overall, when the electric field drives the oxidation of the Ti substrate to $Ti^{4+}$ ions towards the electrolyte, these $Ti^{4+}$ cations are combined with F- ions to form a highly stable complex, i.e., $[TiF_6]^{2-}$. Besides, the migration rate of $F^-$ through the $TiO_2$ anodic film is superior to that of $O^{2-}$ ions and $OH^-$ (from water dissociation). This results in a fluoride-rich metal-oxide interface beneath the anodic oxide film (**Figure 2**) [1, 22, 37].

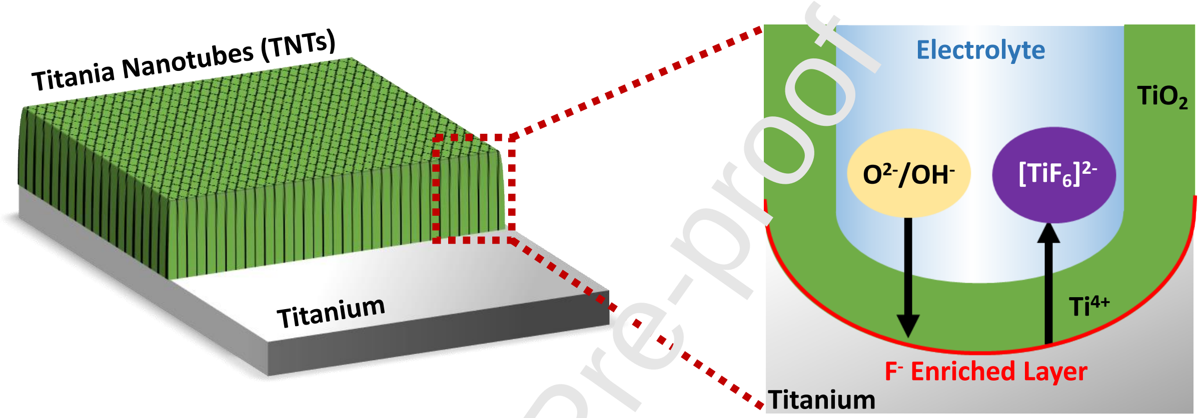


**Figure 2.** Schematic representation of the anodization of titanium (3rd and 4th generations) in fluoride containing electrolyte to fabricate titania nanotubes (TNTs). Adapted from [1, 23].

It is worth noting that recent theories such as *viscous flow* and *electronic current* have reported limitations with respect to the abovementioned traditional theories. These theories showed that the barrier layer grows around the oxygen bubbles at the pore bottom [38-41]. However, the validity of these theories has yet to be established [42-45]. Nevertheless, the electrolyte composition is constantly changing during EA. Further, with repeated EA using the same electrolyte, the concentration of $Ti^{4+}$ and $[TiF_6]^{2-}$ complex increases while the concentration of $O^{2-}$, free $F^-$, $H^+$, $OH^-$ decreases [12]. For instance, A. Valota *et al.* [46], reported a ~40% film growth efficiency in a 0.5 wt% $NH_4F$/glycerol electrolyte at 20 V. This means that 60% of oxidized Ti does not end up in the oxide film (because of chemical dissolution and field-assisted losses). Note that the rest of the cell charge is used in oxygen generation [23, 47, 48].

The electrolyte aging is exclusive to the EA process and is a key factor for developing the TNT layers with a self-ordered morphology [12, 17, 49]. This parameter is well-known in the literature as *electrolyte aging*. This review aims to provide a comprehensive understanding of the aging evaluation and its influence on the characteristics of the anodized nanostructures.

## 3. Electrolyte aging in titanium anodization

During EA, $Ti^{4+}$ ions are continuously released from the Ti substrate to the electrolyte (**Eq. 1**). Simultaneously, the $OH^-$ and $O^{2-}$ anions from hydrolysis are formed. The use of ethylene glycol as solvent favor the formation of $O^{2-}$ (**Eq. 2**) over $OH^-$ (**Eq. 3**) since the volume of $H_2O$ is considerably lower in comparison to ethylene glycol.

$Ti \rightarrow Ti^{4+} + 4e^-$ (**Eq.1**)

$Ti^{4+} + O^{2-} \rightarrow TiO_2$ (**Eq.2**)

$Ti^{4+} + 4\ OH^- \rightarrow Ti(OH)_4$ (**Eq.3**)

By contrast, free F- anions (from $NH_4F$ salt) and $H_2O$ are consumed from the electrolyte upon EA [22, 50]. The presence of $F^-$ and $H^+$ promotes the formation of the porous-like structure by the dissolution of the initial $TiO_2$ compact oxide layer [23]. On that basis, $F^-$ ions in combination with $Ti^{4+}$ cations form a stable and water-soluble complex $[TiF_6]^{2-}$. The formation of this complex is summarized in **Eqs. 4-6**.

$TiO_2 + 6F^- + 4H^+ \rightarrow [TiF_6]^{2-} + H_2O$ (**Eq.4**)

$Ti^{4+} + F^- \rightarrow [TiF_6]^{2-}$ (**Eq.5**)

$Ti(OH)_4 + 6F^- \rightarrow [TiF6]^{2-} + 4OH^-$ (**Eq.6**)

The concentration of this complex in the electrolyte increases over repeated EA (aging), reducing the free F ions. This conditions or ages the electrolyte. Interestingly, it is the presence of free $H^+$ and $F^-$ ions in the electrolyte that maintains the dissolution rate of the $TiO_2$ layer, which is disrupted in aged electrolytes [1, 17]. Therefore, in non-aged (unused or fresh) electrolytes, the equilibrium is shifted towards the dissolution of the oxide layer (**Eq 4**). By contrast, in aged electrolytes, the amount of $H^+$ and $F^-$ is further reduced, thereby shifting the equilibrium towards forming a $TiO_2$ (due to increased formation of $[TiF_6]^{2-}$) (**Eq 4**). According to different studies [12, 51], the pH of the electrolyte increases proportionally as a function of electrolyte aging. However, the neutral pH range (~6-8) has been targeted as optimal to form self-ordered TNT layers.

Because of the chemical changes due to aging, the conductivity of the electrolyte is constantly changing during the anodizing. Interestingly, while some initial aging studies reported an increase in conductivity, in 2015, Gulati *et al.* [8] reported that in an enclosed electrochemical cell (preventing hygroscopic absorption of water into the ethylene glycol-based electrolyte), conductivity reduces with aging. Overall, the electrical conductivity of the electrolyte is related to the concentration of free $F^-$ ions and water in the electrolyte, with both reducing as the electrolyte ages [8, 49]. Further, continuous formation of $[TiF_6]^{2-}$ complexes upon repeated EA also reduces the conductivity of the electrolyte. In another study, Suhadolnik *et al.* [17] monitored the concentration of $NH_4^+$ and water as a function of electrolyte aging and concluded that $NH_4^+$ concentration decreased with aging. However, the standard deviation of the measured values fluctuated considerably, which was attributed to the evaporation of gaseous ammonia during EA. In **Figure 3** we have summarized the key changes in the electrolyte during aging.

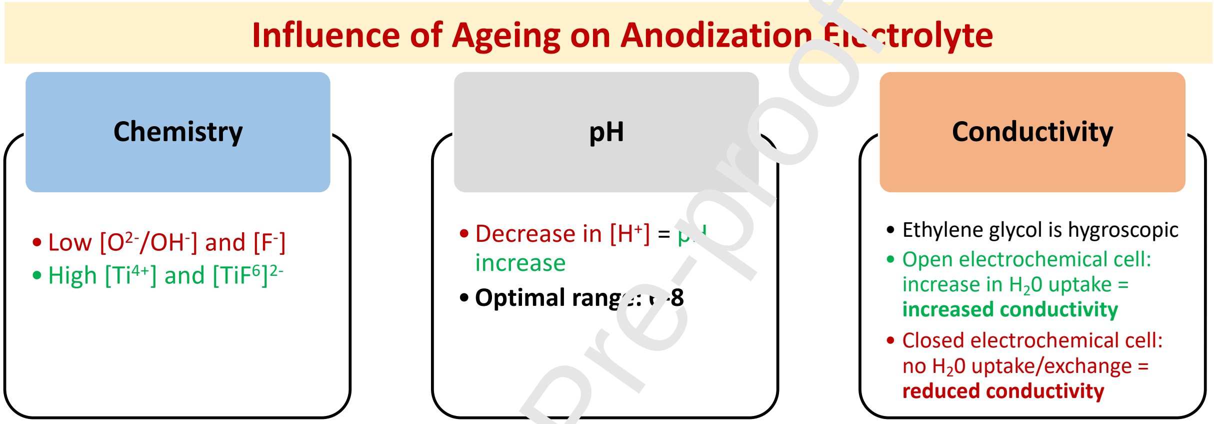


**Figure 3.** Schematic representation of key electrolyte changes after electrolyte aging.

Due to the chemical changes during EA, two different trends in the current density-time curves have been observed in literature: (i) the time to reach the set voltage value (i.e., time to reach the equilibrium); (ii) the maximum current density, and (iii) the stable current value. Regarding the time to reach the set voltage, in a non-aged electrolyte, the higher amount of $H_2O$ results in a lower expansion of the barrier layer, thereby reducing its thickness. Therefore, the initial establishment of the electric field around the anode is favored to meet the set voltage [12, 23]. By contrast, in an aged electrolyte, the establishment of this initial electric field is hindered. Therefore, prolonged treatment times and current density values are needed to achieve the set voltage value [1, 23, 52]. This delay in aged electrolytes may be associated with a thicker barrier layer [12]. As a result, for aged electrolytes, high initial current densities (for constant voltage EA) but delayed time to reach EA equilibrium (stable current value) with relatively higher equilibrium current are observed in comparison with fresh electrolyte, as recently reported by Guo *et al.* [12]. This was associated with a thicker barrier layer since higher current density values at the electrolyte-oxide barrier interface are needed. By contrast, Suhadolnik *et al.* [17] reported a decrease in current density values was observed in aged electrolytes. Note that in both studies the conductivity of the electrolyte and the F- content decreased with aging. Therefore, it may be difficult to establish the influence of electrolyte aging on the fabricated TNT and TNP morphologies. For this reason, depending on the targeted morphology, the aging of the electrolyte needs to be optimized (*See Section 4*).

## 4. Influence of electrolyte age on nanostructure characteristics

### 4.1. Morphology

A critical property that anodized Ti substrates for industrial translation and scalability must meet is the reproducibility and stability of the anodized nano-engineered coating. In this respect, the available literature regarding the effect of electrolyte aging on uniformity of the fabricated nanostructures is scarce. Nevertheless, Suhadolnik *et al*. [17] reported notable differences in the uniformity of the anodized Ti substrates after anodizing in the aged electrolyte. Briefly, Ti was anodized in EG-based electrolyte for 6h at 60V, with one EA performed each day (same electrolyte) and up to 20 days (1, 5, 13 and 20 d; or 0, 24, 72 and 114h, respectively). Since around 5-13 anodized substrates were uniformly modified (**Figure 4**), the authors suggested a 10-20h aging window as most optimized range.

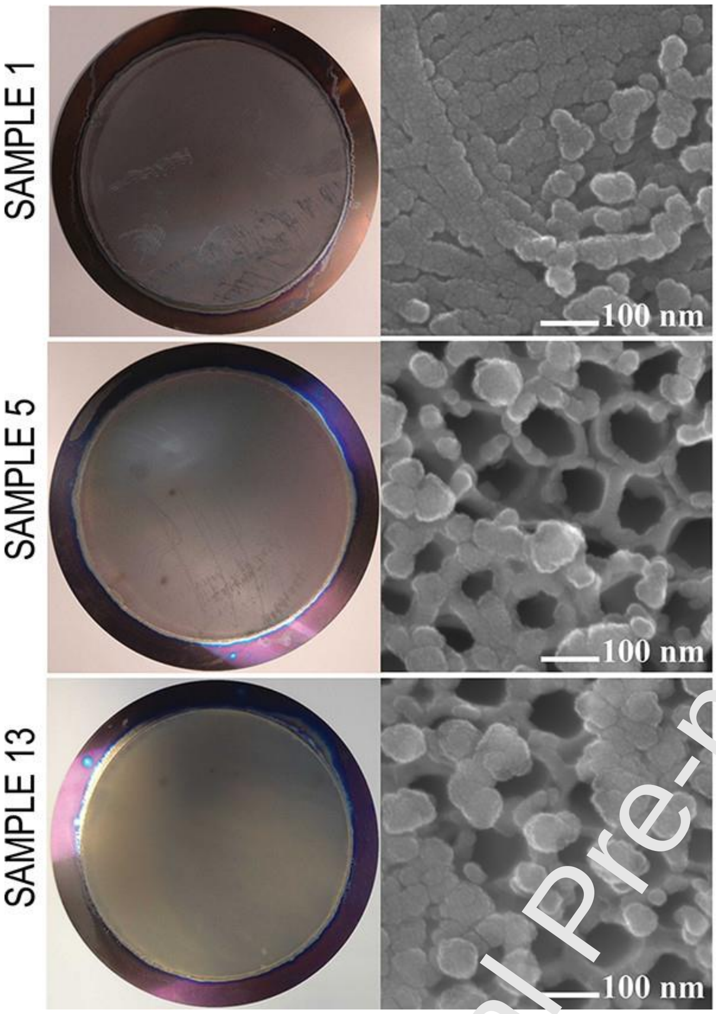


**Figure 4.** Influence of electrolyte aging on the Ti anodization. Photographs and SEM images showing anodized Ti with nanostructures. Samples 1, 5 and 13 are anodized in electrolyte with age 0, 24 and 72, respectively. Adapted with permission from [17].

As can be seen in **Figure 4**, the 5th (electrolyte age: 24 h) and 13th (age: 72 h) TNTs showed a homogeneous surface appearance while the 1st (age: 0h) and 20th (age: 114h) samples were heterogeneous. In this sense, Suhadolnik *et al*. [17] associated these differences with the pH value of the electrolyte. Namely, the pH of the 1st anodization was 5.5 ± 0.3, whereas the pH of the electrolyte used for 20th anodization was 8.5 ± 0.4. This finding is in accordance with several studies where morphologically uniform and consistent TNT arrays usually are formed in a neutral pH range [12, 49].

Besides the more popular TNTs, titania nanopores/TNPs (nanotubes fused together with no inter-tube distance; or nanotubes covered with an initiation layer with nanoscale pores) have also been explored. Representative examples of the effect of electrolyte aging on TNP morphology has been recently reported by several studies [12, 15, 16].

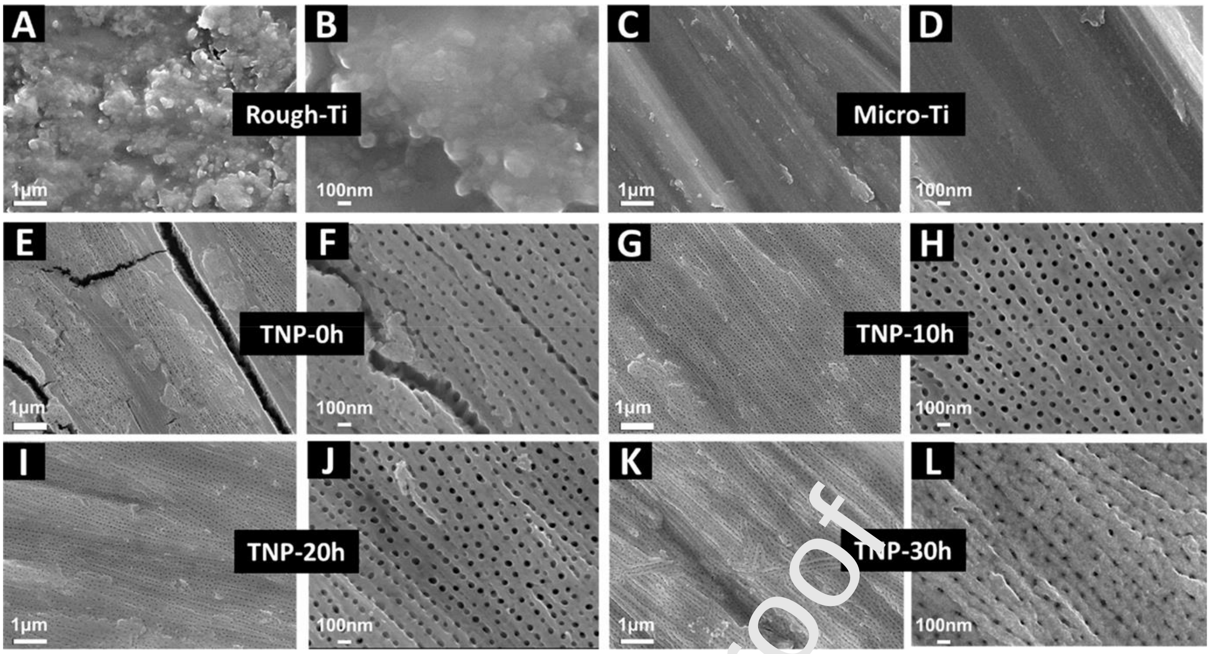


**Figure 5.** Influence of electrolyte aging on titania nanopores (TNPs) made on anodized micro-machined Ti. Top-view SEM micrographs of (a-b) as received Rough-Ti; (c-d) micro-machined Micro-Ti; and (e-l) anodized Micro-Ti with aligned TNPs on Ti (at 60 V, 10 min) using various electrolyte ages (0h, 10h, 20h and 30h). Reproduced with permission from [12].

Guo *et al*. [12] reported fabrication of a stable TNP layer (TNP-10h/20h) on micro-machined Ti when anodized using a 10-20h aged electrolyte (**Figure 5g-j**). These nanopores (TNP-10/20h) were mainly oval/round and well-aligned with the underlying Ti substrate. However, anodizing in over-aged electrolytes (30 h) resulted in the formation of smaller TNPs (**Figure 5k-l**). This morphological change has been also reported by previous studies [16, 49]. Observed phenomenon is attributed to the rapid dissolution of the $TiO_2$ layer by the higher concentration of F- anions in the fresh (unused) electrolyte. This promotes the pore formation, thus consumption of the underlying substrate. By contrast, the higher concentration of $[TiF_6]^{2-}$ complex in aged electrolytes decreases the $TiO_2$ dissolution/formation rate, favoring the ‘conservation’ of underlying substrate topography [16].

Another consequence of electrolyte aging is the reduction in the thickness of the TNT layer. On that basis, the conductivity of the electrolyte is not a decisive factor since controversial results were reported (*see Section 3*). For instance, Sopha *et al.* [49] studied the coating thickness variations as a function of electrolyte aging. The results showed that the TNT growth rate was lower in aged electrolytes. Besides, the length of the TNTs strongly decreased when aged electrolytes were used (**Figure 6**). Note that a decrease in the TNT aspect ratio was observed from ~210 in a fresh electrolyte to ~23 in an electrolyte used for 50

h. This can be attributed to the use of aged electrolyte (lower F- ions) which reduced current density values during the EA process. This was attributed to the concentration in working electrolyte after consecutive anodization.

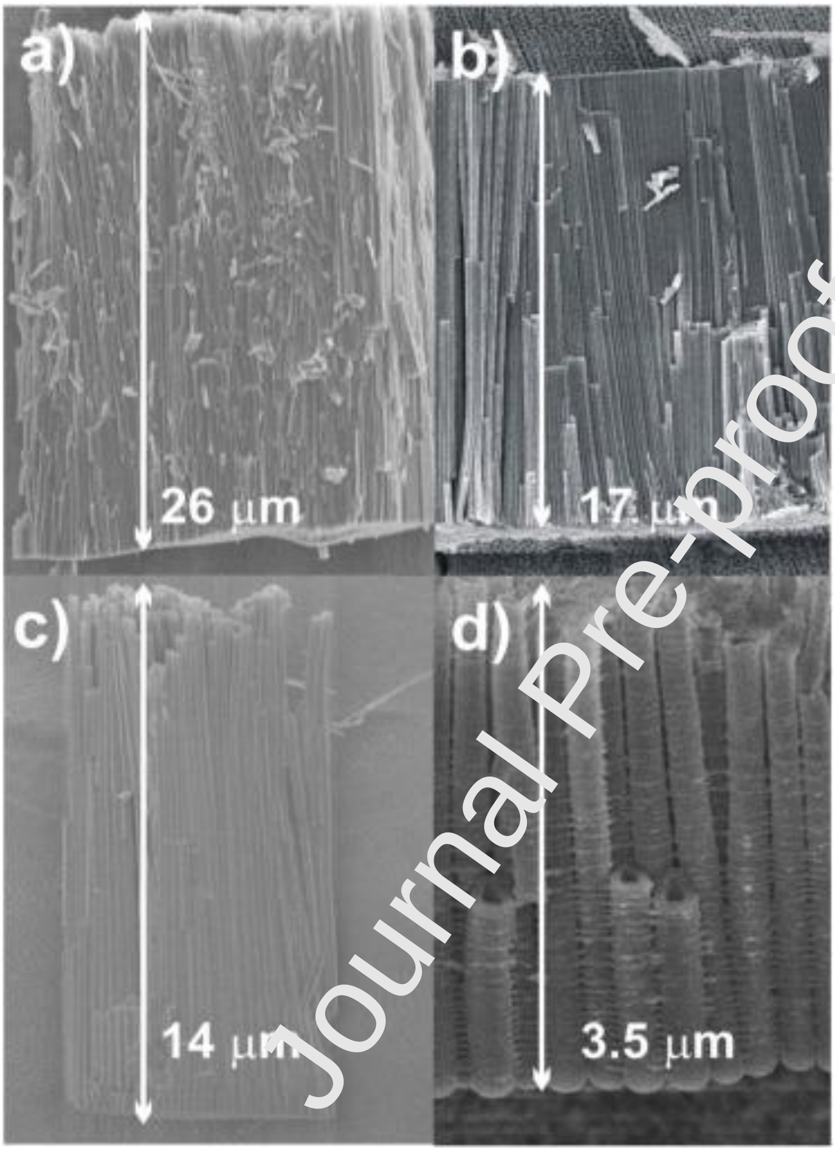
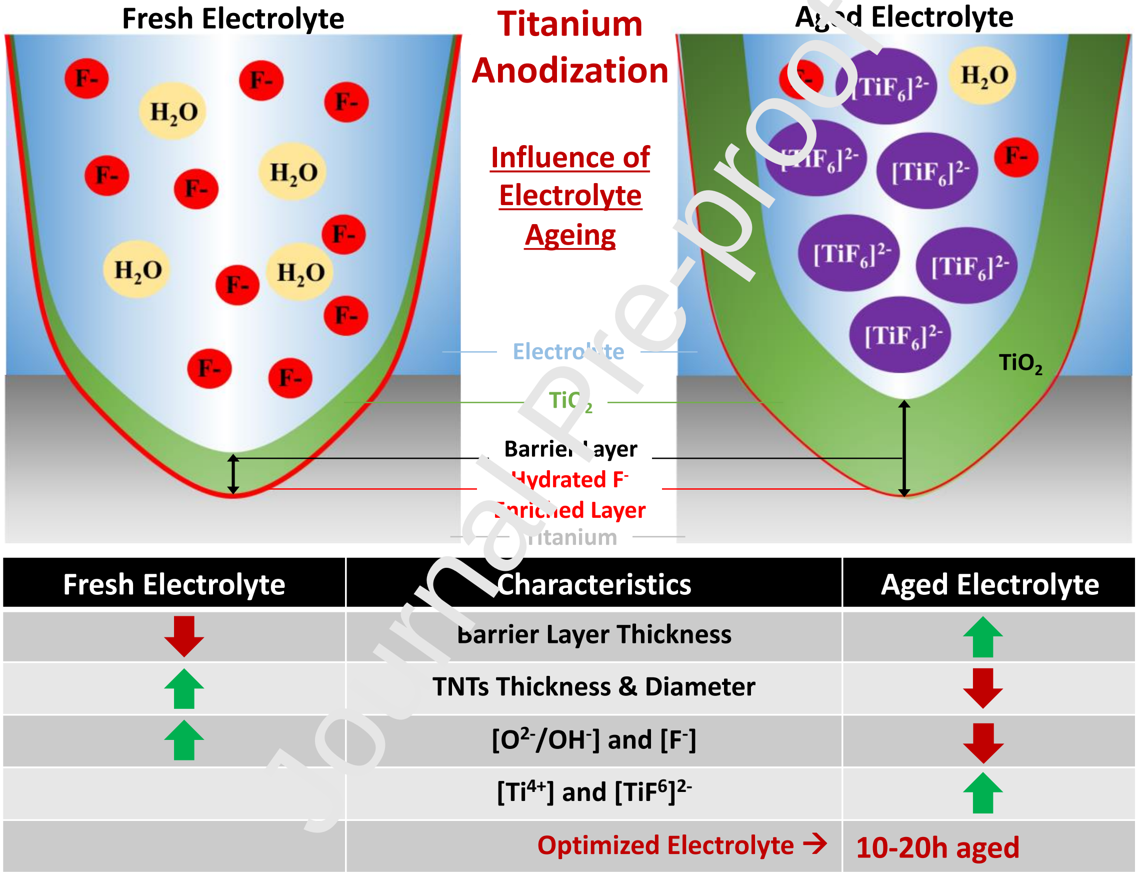


**Figure 6.** Cross-section SEM micrographs of anodized Ti (60 V, 6 h) using different aged electrolytes: a) fresh electrolyte (6 hours), b) 12 hours, c) 31 hours and d) 56 hours. Adapted with permission from [49].

Nevertheless, in the study of Guo *et al.* [12], a non-linear trend of pore diameter and pore density was observed. The authors reported a similar and tiny TNPs were observed for the samples made in the fresh electrolyte and the 30 hours aged electrolyte. Note that the effect of aging is noticeable in both extremes since a significant deviation was reported for both non-aged and over-aged electrolytes. In this context, it is possible to establish an optimal electrolyte aging time to obtain homogeneous TNT/TNP layers in terms of morphology (pore density, pore diameter, uniformity, and thickness), while maintaining reproducibility. According to the available literature, the aging process is usually performed by anodizing a non-target Ti substrate (1 $cm^2$) at 60 V in an ethylene glycol-based electrolyte with 0.088-0.1 M $NH_4F$ and 1-1.5 wt.% $H_2O$ [12, 17, 49]. Thus, the optimal aging time can be established with this procedure in the range of 10-20 hours. **Figure 7** represents the key differences in the electrolyte and the anodization yield (TNPs or TNTs) when an appropriately aged electrolyte is used.



| Fresh Electrolyte | Characteristics | Aged Electrolyte |
|---|---|---|
| ↓ | Barrier Layer Thickness | ↑ |
| ↑ | TNTs Thickness & Diameter | ↓ |
| ↑ | $[O^{2-}/OH^-]$ and $[F^-]$ | ↓ |
|  | $[Ti^{4+}]$ and $[TiF^6]^{2-}$ | ↑ |
|  | Optimized Electrolyte → | 10-20h aged |

**Figure 7.** Anodization of titanium in fresh (unused) and aged electrolyte: key differences in electrolyte chemical balance and the fabricated titania nanotubes (TNTs). Adapted from [8, 12, 17, 49].

### 4.2 Chemistry, Crystallinity and Wettability

TNTs and TNPs are majorly $TiO_2$ with F incorporations from the electrolyte, and hence the use of aged (high Ti-F complexes, reduced active F ions) or fresh electrolyte (minimal/no Ti-F complexes, high free F ions) will influence the chemistry of the nanostructures. However, only two studies have extensively explored the influence of aging on the chemistry and crystallinity of the anodized nanostructures [12, 17]. Suhadolnik *et al*. reported a difference in crystallinity of TNTs fabricated in fresh electrolyte EA, which showed that peaks for anatase $TiO_2$ reduced for TNTs fabricated in aged electrolyte (more aging: less anatase) [17]. However, it is worth noting that the aging was performed for many days, at 60V for 6h each day for 1, 5, 13 and 20 d (or 0, 24, 72 and 114h, respectively). In a recent attempt by Guo *et al.*, four electrolytes were made: fresh, and 10, 20 and 30h aged electrolytes (aged using 80V) [12]. EA of micro-machined Ti substrates led to the formation of aligned nanopores, which were investigated for chemical composition (XPS), crystallinity (XRD) and hydrophilicity (water contact angle). XPS indicated that F was slightly reduced with electrolyte aging. Interestingly, both XPS and XRD did not yield any statistically significant differences between the anodized groups (all electrolytes). Hydrophilicity can dictate protein and cell adhesion, and the study reported the hydrophilicity trend: 30h > 20h >10h = 0h (fresh) > controls (non-anodized Ti). It was suggested that the hydrophilicity was influenced by both, chemistry and topography of the nanopores. This was attributed to the smaller pore size of nanopores anodized using an over-aged (30h) electrolyte. Please note, in comparison with Guo *et al.* [12], Suhadolnik *et al.* [17] performed aging at 0, 24, 72 and 114h, hence could obtain significant difference in the XRD data.

### 4.3 Mechanical Stability

The stability and robustness of the anodic nanostructures are crucial, irrespective of the application, as any delamination or breakage may result in malfunction. This is particularly crucial in a biomedical implant application, whereby, the anodized Ti implant surface may be subjected to repeated mechanical loading cycles over the years [53]. It is also noteworthy that biomedical implants (orthopaedic and dental) involve implants of complex shapes and geometries, often with micro-roughness, and hence to ensure stability and survival under-load, various attempts have been made to augment the stability of nanotubes, as reviewed elsewhere [50].

Mechanical properties of the anodized Ti (influence of electrolyte aging) are mostly qualitatively assessed via imaging (SEM) or quantitively via nanoindentation (to measure hardness and Young's modulus). Electrolyte aging influences the rate of $TiO_2$ formation and its dissolution, and the time to reach anodization equilibrium (teq). This not only dictates the 'consumption or conservation' of the micro-topographical features of the underlying substrate but also the adherence of the anodic film on the substrate [16]. It is also worth noting that nanostructures on 'conserved' underlying micro-topography are mechanically more stable than the ‘consumed’ micro-topography or anodized polished substrates [54]. However, studies have shown that rougher substrate leads to a more homogenous anodic film, while polished ones can lead to irregular morphology. On the other hand, these studies did not investigate or disclose the electrolyte aging [55]. In 2015, Gulati *et al.* reported that anodization of electropolished and smooth Ti wires (75V 10min) using fresh electrolyte yields severely compromised (cracked and easily delaminated) anodic film [8]. While for 10h aged electrolyte (aged at 75V), stable anodic film was formed using the same substrate and conditions. As recently reported for anodization of curved substrates, the cracks or pits on anodic film may be unavoidable due to curvature, internal stresses (uneven electric field distribution), oxide volume expansion, collapse of nanotubes, and the presence of weak spots [55-57]. Hence, for complex or curved Ti substrates, the aged electrolyte may be a more suitable solution to reduce the anodic film cracking, pits and inconsistencies [15, 58].

Surface topography of the underlying substrates can also dictate the ordering of the TNTs/TNPs, hence the anodize-remove-anodize technique (well-known as two-step anodization) forms hexagonally arranged TNTs on the nanotemplate [59]. In 2018, Li et al. used irregular-rough (Rough-Ti) and micro-machined rough (Micro-Ti) Ti as a substrate, and anodized it with fresh or aged (75V for 10h) electrolytes at 60V for 10min, and observed compromised and unstable anodic film for fresh EA (only for first anodization) (**Figure 8**) [15]. Note that aged electrolyte is an important consideration specially for anodizing clinical implants, as they often come in complex geometries and micro-roughness [60]. Further, the formation of aligned (first EA on Micro-Ti) and random ($2^{nd}$ EA on nanotemplate) nanopores with appropriate anodic film attachment was shown for dental implants (screws and abutments) [15].

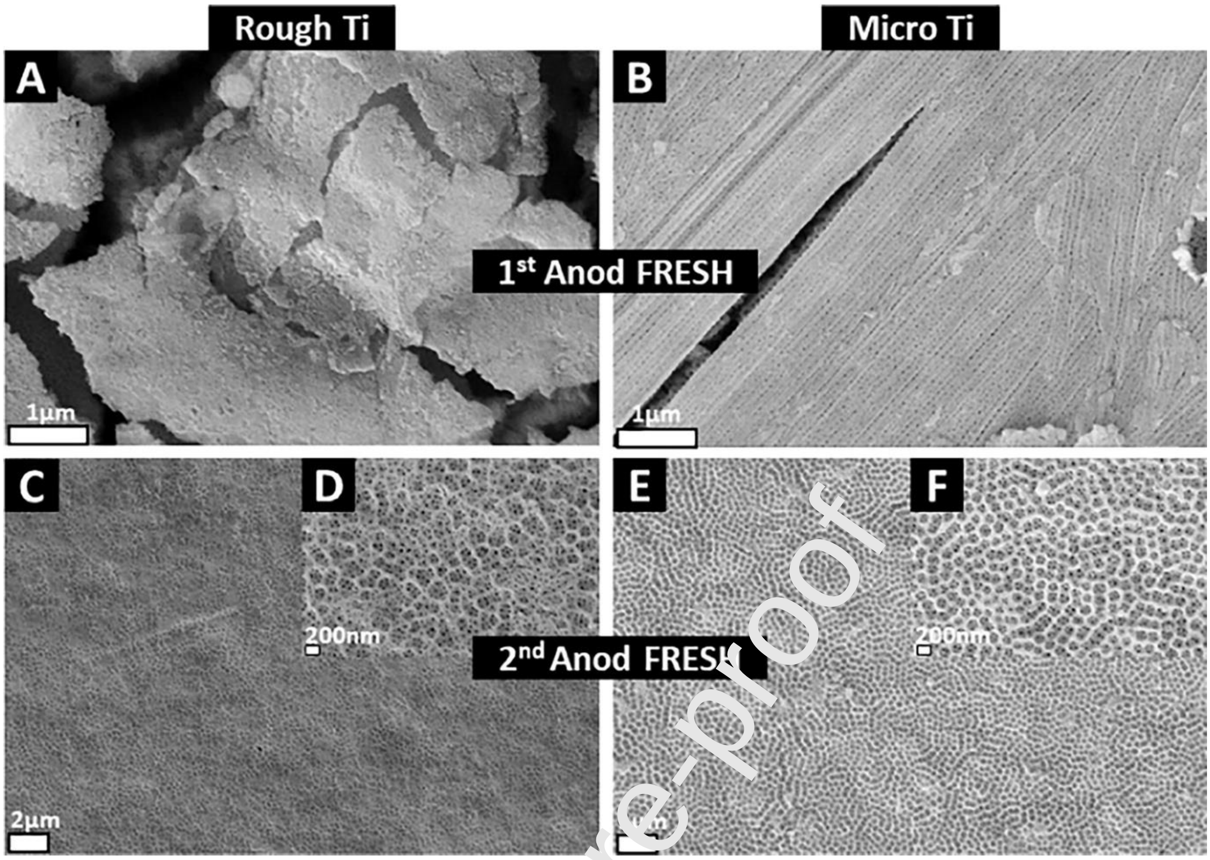


**Figure 8.** Cracking in anodic film in fresh electrolyte anodization. Top-view SEM images: (A-B) showing the cracked anodic film on irregular rough (Rough-Ti) and micro-machined rough (Micro-Ti) substrates upon anodization with fresh/unused electrolyte. (C-F) for second anodization (remove first anodic film and re-do anodization), no cracks were observed. Adapted with permission from [15].

Further mechanical investigations have revealed that (1) electrolyte aging augments stability of nanotubes on curved surfaces [8] and commercial implants [15]; and (2) nanopores fabricated using aged electrolyte demonstrate increased hardness and elastic modulus values on flat micro-rough Ti [12, 16, 58, 61] and curved Ti wire [15]. Such observations have been attributed to aging-induced delay in reaching EA equilibrium, thicker barrier layer, and reduced cracks and porosity (for nanopores) for aged anodization. The nanoindentation findings for aged electrolyte fabricated TNPs have revealed enhanced Young's modulus and hardness values for a similar indentation depth, which translates into augmented stability and mechanical robustness [12]. The authors have also reported reduced cracks on TNPs fabricated in aged electrolytes. It is noteworthy that enhanced chemical dissolution in aged electrolyte EA can aid in dissolving surface aggregation parts and thereby reducing internal stresses (at the barrier layer – Ti substrate interface) [9]. This in turn significantly augments the adhesion between the TNTs and the underlying Ti substrate, which can improve application specific performances like photoelectrochemical properties.

### 4.4 Application specific performance and future directions

***Implant bioactivity***

Owing to high nanoscale roughness, enhanced bioactivity and ability to load/locally elute potential therapeutic agents, anodized Ti nanostructures including nanotubes and nanopores hold great promise as the next generation of orthopaedic and dental implants [62, 63]. As a result anodized Ti implants have been extensively utilized as promotors of implant-tissue integration [64] and therapeutic modifications [65], as established by numerous *in vitro* and *in vivo* investigations [66, 67]. Further, TNTs or TNPs fabricated using aged electrolytes can have significantly altered morphology, chemistry and stability, which in turn dictates protein adhesion and cellular functions [68, 69]. In a recent study, Guo *et al.* reported the untwining of the chemistry-topography interdependence and its influence on the bioactivity of TNPs on micro-rough Ti [70]. More recently, it was also shown that anisotropic nanopores fabricated on Micro-Ti (micro-machined) using controlled aged EA mechanically stimulates cells (osteoblasts and fibroblasts) and enables their parallel alignment to the nanopores starting at 24h [58, 61].

In a pioneering attempt, Guo *et al.* reported that electrolyte aging influences the bioactivity of the fabricated aligned nanopores on anodized micro-machined Ti [12]. While differently aged electrolytes (fresh, 10h, 20h and 30h) were used to fabricate aligned TNPs, no significant difference in protein adhesion was observed among the TNP groups. Next, human gingival fibroblasts (hGFs) were cultured on the different substrates *in vitro* and the findings revealed that TNP-20h outperformed other TNPs and enabled the highest viability (day 1) and enhanced hGF proliferation (days 1 and 3). At further time-points, TNP-20h and TNP-10h showed similar favourable responses. This was attributed to the improved preservation of the underlying substrate micro-roughness and formation of uniform nanostructures for EA performed with 10/20h aged electrolyte. For the cell spreading morphology, TNPs fabricated using aged electrolyte showed more extensive axial stretching, indicating mechanotransduction from the well-aligned nanopores. The study concluded that 10-20h aging is the most appropriate to achieve enhanced bioactivity from anodized implants.

It is noteworthy that aging influences TNTs' diameter, length and ordering, which in turn can control the available vacant volume for drug loading and release [71], however, this has not been explored with respect to electrolyte aging [67] [65]. Further, as mentioned previously, most studies encompassing TNTs/TNPs application towards biomedical implants may utilize aged electrolyte towards their fabrication, but the influence of aging on TNTs/TNPs modified implants needs further investigations.

### *Photocatalytic activity*

Besides biomedical implants, TNTs have also been widely optimized towards their photocatalytic applications [3, 72, 73]. Over the last few decades, $TiO_2$ has been widely researched as a photocatalytic material, attributed to its outstanding electronic properties [74]. Review by Paramasivam et al. details the photocatalytic applications of TNTs, along with strategies to enhance its photocatalytic performance [73]. In 2011, Zhu *et al.* reported increased photoelectrochemical properties (higher photocurrent densities) of the TNTs fabricated in aged electrolytes [9]. This enhancement was attributed to the effect of the electrolyte aging in improving the adhesion of TNTs to the underlying Ti substrate and their well-ordered morphology. This improved adhesion translates into a better connection between the TNTs and Ti substrate, thereby reducing the boundary defects. The authors also reported that TNTs developed in aged electrolytes 3 vol.% water content demonstrated maximum photoactivity.

More recently, Suhadolnik *et al.* reported the influence of EA electrolyte aging on the photocatalytic activity of TNTs [17]. Ti was anodized for 6h at 60V, with one EA performed each day (same electrolyte) and upto 20 days (1, 5, 13 and 20 d; or 0, 24, 72 and 114h, respectively). Only 5 and 13d TNTs displayed open pores, while 0 and 20d had closed pores. Next, the photocatalytic activity of the TNTs was determined using caffeine degradation during UV illumination (3h) and it was found that TNTs fabricated in 1d and 5d aged electrolyte showed a 60% degradation of caffeine. However, both 13d and 20d TNTs displayed relatively poor photocatalysis, with only 44% of caffeine degradation, after the longest reaction time.

### *Dye-sensitised solar cells (DSSCs)*

TNTs can be used to achieve vertically oriented fast electron pathways, and hence have been widely applied as Grätzel-type dye-sensitized solar cells (DSSCs) [75]. Optimizations in Ti anodization has permitted fabrication of high-aspect ratio and smooth tube wall TNTs, which has significantly improved their solar cell performance [76]. However, only one study has investigated the influence of aging on the performance of TNTs as DSSCs. Lee *et al.* investigated the applicability of TNTs fabricated in fresh and aged electrolyte (conductivities

40 μS/cm and 80 μS/cm, respectively) towards dye-sensitized solar cells [10]. It was reported that aged electrolyte (high conductivity) had the highest cell efficiency (2.64%). Further, the longer TNTs and well-ordered structuring obtained in aged electrolyte EA attributed to the higher efficiency (which depends on the chemisorbed area between the dye and TNT anode). Next, smaller charge-transfer resistance from aged EA TNTs was also observed.

### *Future directions in electrolyte aging*

The performance of the abovementioned applications can further be enhanced if electrolyte aging and Ti anodization is further optimized, yielding controlled, stable, and reproducible nanostructures. The following are key future directions in this domain, ensuring ease of industrial translation, matching specific application needs:

- ***Additional parameters.*** Towards electrolyte aging, the influence of time on electrolyte conditioning is reported in various studies. However, understanding the influence of alternate EA parameters like anode area and voltage can further shine light on optimizing the aging process.
- ***Short-time anodization***. Often for the aging experiments, time of anodization is several minutes or hours. Further, aging corresponds to varied substrate features (like rough or ordered micro-roughness). Precise influence on the generation of self-ordered nanostructures can be estimated via studying short-time anodization in various aged electrolytes. Investigating few seconds of anodization under varied electrolyte ages can address this knowledge gap.
- ***Complex substrate roughness/geometry.*** As discussed in the review, applications require specific substrate shape, geometry and roughness. For instance, biomedical implants exist as screws, plates or pins, often with micro-roughness. While it is now possible to anodize with preserved substrate features (dual micro-nanostructures), further developments would arise, if precise influence of aging is explored across various complex substrate types – like curved surfaces with micro-roughness.
- ***Electrolyte aging in other metals.*** It is established that over 21 metals and semi-metals and several alloys can be nano-engineered via anodization. However, the research encompassing influence of electrolyte aging is primarily restricted to Ti. It remains unexplored if the electrolyte aging contributes to improved nanostructure ordering and stability in anodization of other metals.

## 5. Conclusions

When titania nanotubes or nanopores fabricated via electrochemical anodization of Ti (in organic electrolytes, especially ethylene glycol-based) showed enhanced stability upon fabrication in the several times used electrolyte, the concept of electrolyte aging was conceived. Repeated anodization using non-target Ti conditioned the electrolyte (changing the chemical balance of water and free fluoride ions) and tuned its characteristics, including reduced electrical conductivity, reduced water and free fluoride content, and increased pH. This chemical change influenced the characteristics of the fabricated nanostructures, including morphology, chemistry, stability and also application-specific performances (towards dye-sensitized solar cells, biomedical implants and photocatalysis). This pioneering review presented a summary of the key findings in the domain of electrolyte aging in Ti anodization, comparing the research performed so far, and informing the reader of the research gaps. Further advances in this metal nano-engineering platform can happen via optimization of aging via tuning other parameters (voltage and anode area), short-time anodization of varied substrate geometry/roughness and ultimately evaluating the influence of aging on other metals (that can be nano-engineered via anodization). Clearly, electrolyte aging for Ti in organic solvents (with fluoride and water) is one of the neglected yet frequently used technique to fabricate controlled nanostructures with reproducible morphology and appropriate stability towards varied applications.

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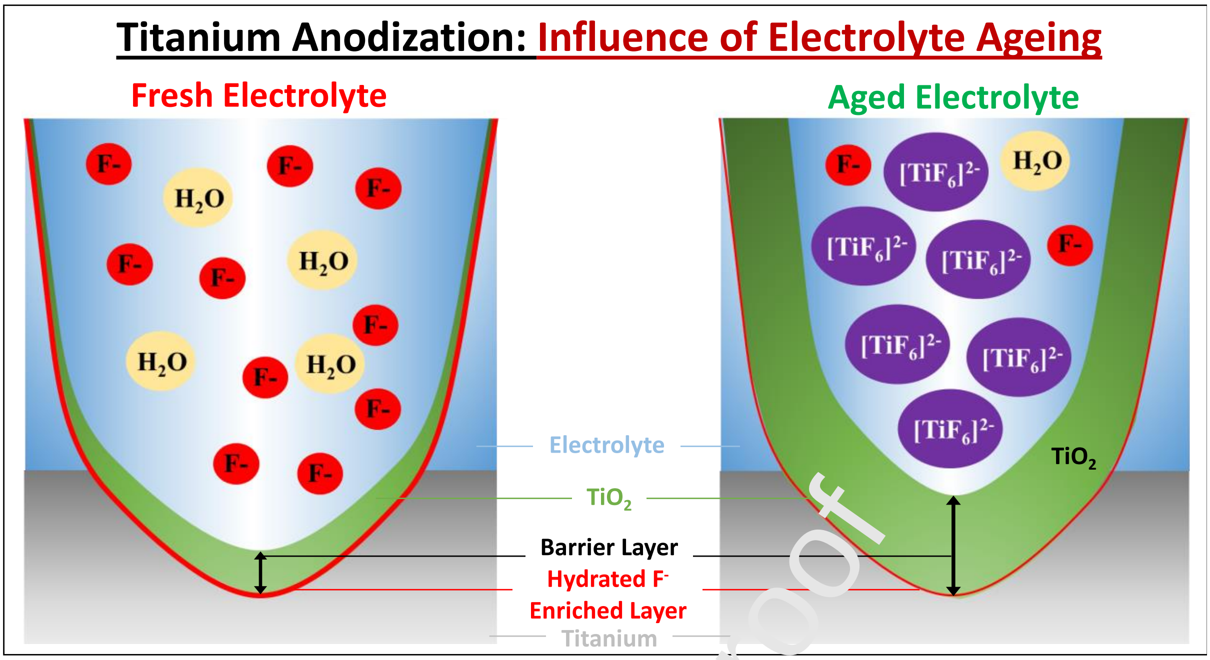
Titanium Anodization: Influence of Electrolyte Ageing
Fresh Electrolyte
Aged Electrolyte
F-
H$_2$O
[TiF$_6$]$^{2-}$
TiO$_2$
Electrolyte
TiO$_2$
Barrier Layer
Hydrated F$^-$
Enriched Layer
Titanium

# Highlights

- Anodization of Ti enables fabrication of $TiO_2$ nanostructures for varied applications
- Electrolyte ageing involves repeated use of same electrolyte prior to anodizing target Ti
- Ageing of organic electrolytes is routinely practised for Ti anodization but seldom reported
- This review discusses and details the basics and advances in electrolyte ageing
- Influence of ageing on the characteristics and performance of $TiO_2$ nanotubes is discussed

## Declaration of interests

☒ 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.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: