Wireless Anodization of Ti in Closed Bipolar Cells

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In this work, the anodization of Ti foils in closed bipolar cells is shown for the first time. Depending on the applied potential, i.e. direct or alternating potential, TiO_2 nanotube (TNT) layers can either be prepared on one side or on both sides of a Ti foil. It is shown that due to the use of closed bipolar cells, potentials with different amplitudes can be applied within the individual two half-cells. Additionally, different electrolytes can be used for the anodization of the two sides of a Ti substrate. Thus, the TNT layers obtained under alternating potential on both sides of a Ti foil can have completely different dimensions, i.e. TNT diameter and TNT layer thickness. Furthermore, by employing alternating potentials, black TNT layers can be synthesized on the side of the Ti foil, while being reduced during the last anodization step at negative potentials.

Since Honda and Fujishima[1] showed the possible use of TiO_2 for water splitting in 1972, tremendous research has been carried out on this material which is nowadays used in various applications.[2–4] In the last decades the focus of these studies has been devoted on TiO_2 nanomaterials, for instance nanoparticles,[5] nanotubes[6] or nanofibres,[7] owing to their large specific surface area. Among these nanomaterials, anodic TiO_2 nanotube (TNT) layers have gained tremendous attraction due to manifold advantages compared to other nanomaterials, such as flexibility on dimensions and structure, easy and low-price production, or their direct fabrication on Ti substrates yielding a conductive back contact, unique tubular geometry, allowing a fast electron pathway along the nanotube walls and optimal light absorption.[4,8] In the early 2000s, intensive studies were carried out on electrolyte composition[9–14] as well as on the influence of the anodization potential and time on TNT diameter and TNT layer thickness.[15,16]

Conventionally, anodic TNT layers are produced in a two-electrode set-up, using the Ti substrate as an anode, while a Pt, carbon or even a second Ti substrate serve as counter electrode.[4,8] In this set-up, a Ti substrate can be decorated with TNT layers all around, if immersed completely into the electrolyte. Alternatively, it is possible to anodize just one side or parts of the Ti substrate by insulating the part of the substrate that should not be anodized or by pressing the Ti substrate against an O-ring of specially designed electrochemical cells exposing just one side or a part of the substrate to the electrolyte. However, in such set-ups it is not possible to produce different kinds of TNT layers (i.e. differing in nanotube diameter and layer thickness) on the two sides of the Ti substrates during one anodization experiment. Additionally, small Ti objects cannot be anodized as they cannot be electrically connected to the potentiostat.

In 2014, the use of bipolar electrochemistry for the fabrication of TNT layers in open anodization cells was introduced.[17,18] In a bipolar electrochemical set-up, the Ti substrate acts as bipolar electrode (BPE) in between two feeder electrodes inserted into a suitable electrolyte. The electrical potential is applied to the feeder electrodes, while the BPE is not directly connected to the potentiostat. Instead, it is polarized by the electrical field between the feeder electrodes.[19,20] Consequently, the part of the BPE facing the feeder cathode is the anodic pole of the BPE and oxidation reactions are induced on this side of the BPE. On the other side of the BPE, facing the feeder anode, reduction reactions are induced, as this side is cathodically polarized.

By using bipolar electrochemistry in open anodization cells, somewhat over half of the BPE's surface area can be anodized, however, not the whole surface area due to the fact that one end is cathodically polarized.[17,18,21] Moreover, in this configuration a gradient in nanotube diameter and nanotube layer thickness along the BPE can be found due to the changes in the electrical field along the BPE.[17,18,22–24] To overcome these problems, the application of an alternating potential between the feeder electrodes was introduced for the synthesis of Al_2O_3 nanopores[25–28] and TNT layers.[29] The use of an alternating potential leads to the formation of nanopores or nanotubes, respectively, along the whole BPE as both ends of the BPE are alternately positively polarized. However, naturally also by applying alternating potentials gradients in the diameter and thickness of the nanotubes along the BPE can be observed.[29]

A possible alternative to the use of open cells for bipolar electrochemistry are so-called closed cells.[30,31] In this configuration, a two-compartment cell, consisting of two half-cells, is used with the electrolytes separated by the BPE (Scheme 1). The feeder electrodes are each in one of the half-cells. This set-up

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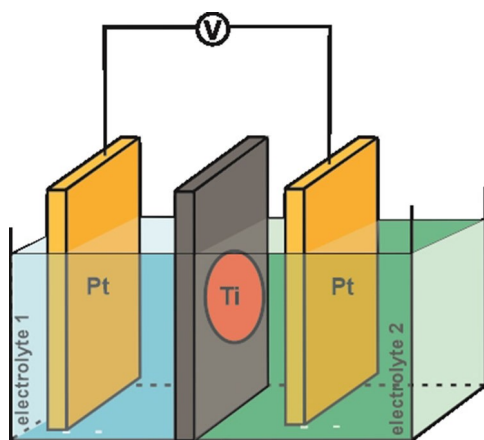*E-mail: hannaingrid.sopha@upce.cz*

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doi.org/10.1002/celc.202100799

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Scheme 1. Set-up of the closed bipolar cell. Yellow – Pt feeder electrodes, red – Ti foil, grey – Teflon wall separating the two-half cells and containing the Ti foil between two O-rings.
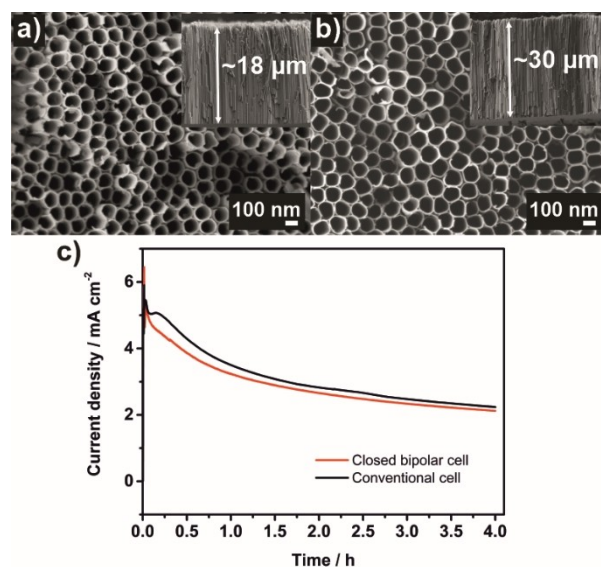

Figure 1. SEM images of TNT layers prepared in a) the bipolar cell, and b) the conventional cell applying a direct potential of 60 V for 4 h. c) Current density-time curves obtained for both anodizations.

has the advantage that the applied potential is not dependent on the size of the BPE, as all the current must solely flow through the BPE. Such a set-up is analogous to two electrochemical cells coupled in serial connection and the potential on the BPE is the same as the potential applied between the feeder electrodes.[31] Furthermore, two different electrolytes can be used in the two half-cells.[30] This means that the two sides of the BPE can be modified in different electrolytes. In the particular case of anodization of Ti substrates, both sides of the Ti substrate can be modified with TNT layers of completely different dimensions.

Such closed bipolar cells were recently used for the anodization of Al.[32] The authors used a closed bipolar set-up consisting of two beakers and a bent Al sheet as bridge, each end of the sheet immersed into one beaker. By applying a direct potential, the end of the Al sheet facing the feeder cathode was anodized and porous Al_2O_3 was formed.

In the work herein, we use a similar, yet different set-up, for the anodization of Ti foils. The Ti foil was placed between two Teflon walls of the electrochemical cell, directly between the two half cells, as shown in Scheme 1. In this configuration, both sides of the Ti foil, i.e. 1.77 cm² each, are in direct contact with the electrolytes. It is shown that by applying a direct potential, just the side facing the feeder cathode is anodized and TNT layers are formed. On the other hand, by applying an alternating potential, both sides of the Ti foil can be anodized. Depending on the applied potentials and used electrolytes, TNT layers with either identical or with completely different dimensions can be grown on both sides of the Ti foil.

Figure 1 shows TNT layers obtained in the closed bipolar cell (Figure 1a) and in a conventional cell (Figure 1b) upon anodization in ethylene glycol-based electrolyte containing 170 mM NH_4F and 3 vol% H_2O (EG-based electrolyte) at 60 V for 4 h. For the closed bipolar cell, the EG-based electrolyte was used in both half-cells. As one can see, homogeneous TNT layers were obtained in both types of cells with very similar TNT diameters, i.e. 119 ± 12 nm and 130 ± 15 nm for the bipolar and conventional cell, respectively. As described in the literature,[4,8]

the nanotube diameter is influenced by the applied potential. Thus, the fact that similar diameters were received herein for the conventional and the closed bipolar set-up, confirms that the potential on the Ti foil in the closed bipolar cell is equal to the one applied in the conventional set-up to the Ti foil, i.e. 60 V.

However, the TNT layer was comparably thinner in case of the bipolar cell. This is in accordance with the recoded current density-time plots, shown in Figure 1c, which show that slightly higher current-densities were obtained in case of the conventional cell which in consequence results in slightly higher growth rates of the TNT layers.[8] As electrolytes of the same composition and exactly the same age were used for the anodization in both set-ups,[33,34] the reason for the differences in recorded current density and TNT layer thickness are most likely connected to the relatively low conductivity of the EG-based electrolyte, which was used also in the half-cell with the feeder anode for the bipolar set-up. On the other hand, in the conventional set-up, the Ti foil is directly connected to the potentiostat. Thus, a higher IR drop is expected for the bipolar cell. Similar results were found by Xu et al.,[32] who showed in their study on the anodization of Al in a closed bipolar cell that using an electrolyte with higher conductivity in the half-cell containing the feeder anode resulted in thicker porous Al_2O_3 layers compared to electrolytes with lower conductivity.

To gain more insights into the anodization of Ti foil in the bipolar cell, alternating potentials were applied between the two feeder electrodes resulting in TNT layer formation on both sides of the Ti foil. Figure 2 shows the TNT layers obtained when potentials of ± 60 V with different frequencies for a total time of 6 h were applied, when both half-cells contained the same EG-based electrolytes. The applied frequencies were in the range between 0.067 Hz and 9.26×10^{-5} Hz, corresponding to anodization times between 15 s and 3 h before the direction

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doi.org/10.1002/celc.202100799

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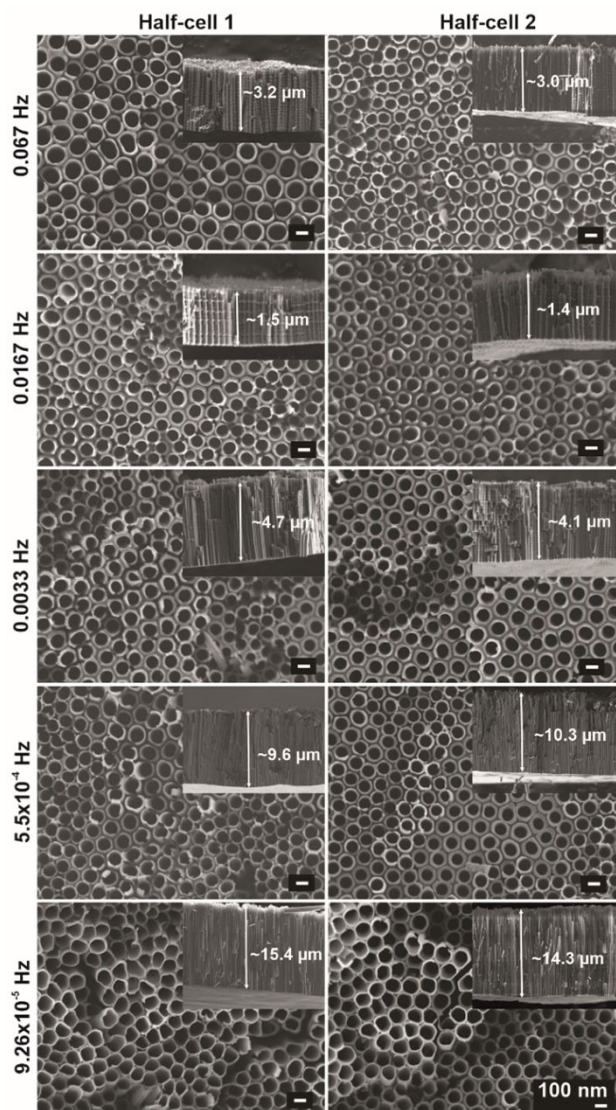European Chemical
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Figure 2. SEM images of TNT layers obtained in a closed bipolar cell on both sides of the Ti foils using alternating potential of different frequencies with an amplitude of ± 60 V for 6 h in total. EG-based electrolyte was used in both half-cells. The scale bars show 100 nm.
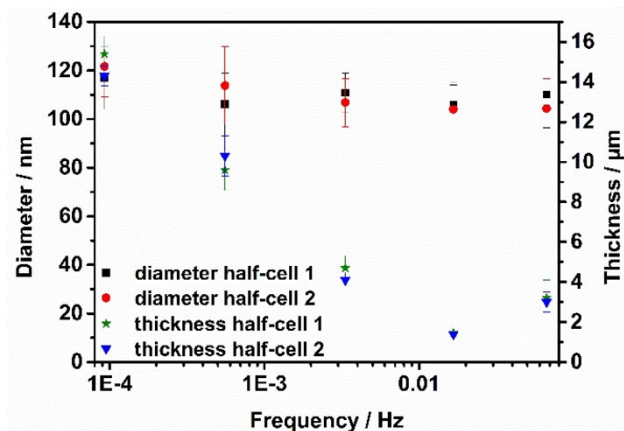

Figure 3. Dependency of the diameter and thickness of the TNT layers on the frequency of the applied alternating potential of ± 60 V for 6 h.

of the potential was changed. Table S1 summarizes the anodization conditions. As one can see in Figure 2, well developed and homogenous TNT layers were obtained in both half-cells for all used frequencies with the diameter being independent from the frequency of the alternating potential. This can be expected as it is known from the literature that the diameter is mostly dependent on the anodization potential, but not on the anodization time.[4,8,34]

The dimensions of the TNT layers obtained on both sides of one Ti foil were practically identical for all frequencies, as displayed in Figure 3. The TNT layer thickness, however, was strongly influenced by the applied frequency, as can be seen in Figures 2 and 3. An almost linear increase of the TNT layer thickness was observed, when the frequencies were decreased. Thus, the thickest TNT layers were obtained when a very low frequency of 9.26×10^{-5} Hz was applied, which in fact means

keeping the potential for 3 h at $+60$ V before changing to -60 V. In this case, both TNT layers were synthesized after each other, first on one side, then on the other side. As the TNT layers on both sides of the Ti foil reveal the same thicknesses, it shows that the adhesion of the TNT layers to the substrate is good and the TNT layers did not lift of during reduction. In contrast, the shortest TNT layers were obtained for a frequency of 0.0167 Hz, corresponding to holding the potential constant for 1 min, before changing the direction. Interestingly, for a frequency of 0.067 Hz thicker nanotube layers were observed than for a frequency of 0.0167 Hz. The reason for this is not entirely clear yet, however, it might be due to the extremely short cumulative anodization times of 15 s, before the potential direction is changed. In this short time, equilibrium conditions are not yet reached, thus it might not be enough time given to the fluoride ions in the electrolyte to migrate to the surface of the TNT layer. As a consequence the etching of the TNT layer surface might be less strong.[8]

Having a look at the cross-section SEM images in Figure 2, one can observe very regular ripple formation (also known as bamboo-like structure) along the TNT layers, especially when higher frequencies were applied. Although this was not investigated in detail in this study, it is expected that the ripples are formed due to the use of the alternating potential and appear every time the potential direction was changed. The same phenomenon was observed by Albu et al. during application of an alternating potential in a conventional set-up in HF based electrolyte.[35]

It must be noted that the side being reduced during the second half of the last anodization cycle revealed a darker color than the side being anodized at the same time. In case of very low frequencies, when one side of the Ti foil was reduced for 30 min or even 3 h before being taken out of the anodization cell, this side was found to be of deeply black color (see also Figure S1). This is in particular interesting, as the reduced TiO_2 containing high amounts of Ti^{3+} species, so-called black titania, recently gained tremendous interest, as it shows remarkable visible light photocatalytic water splitting performance.[36,37]

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doi.org/10.1002/celc.202100799

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Thus, XPS was carried out on the TNT layers on the Ti foil being anodized with a frequency of 9.26×10^{-5} Hz (Figure S2). When applying this frequency, the Ti foil was anodized on one side for 3 h before the potential direction was changed and the other side was anodized. Thus, the TNT layer on the firstly anodized side was reduced in the ethylene glycol-based electrolyte for 3 h, while the TNT layer on the side anodized last was not reduced at all. The results show that the amount of Ti^{3+} found in the reduced TNT layer was substantially higher than in the non-reduced TNT layer on the other side of the Ti foil. Thus, the TNT layer was strongly reduced, showing a possible way to produce black TiO$_2$. Please note that some minor amount of Ti^{3+} can always be found in the TNT layers produced by anodization due some lattice defects.[38,39]
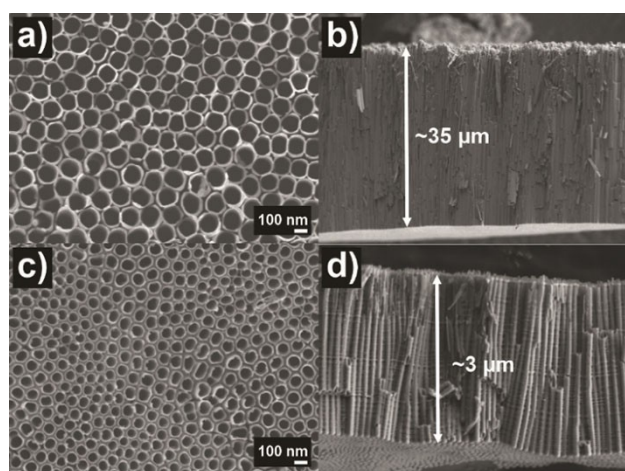

Figure 4. SEM a, c) top view and b, d) cross-sectional images of TNT layers obtained in a closed bipolar cell on both side of the Ti substrate using alternating potential of a frequency of 5.6×10^{-4} Hz (changing the potential direction every 30 min) with an amplitude of $+80$ V in half cell 1 (a, b) and -40 V in half cell 2 (c, d). EG-based electrolyte was used in both half-cells.
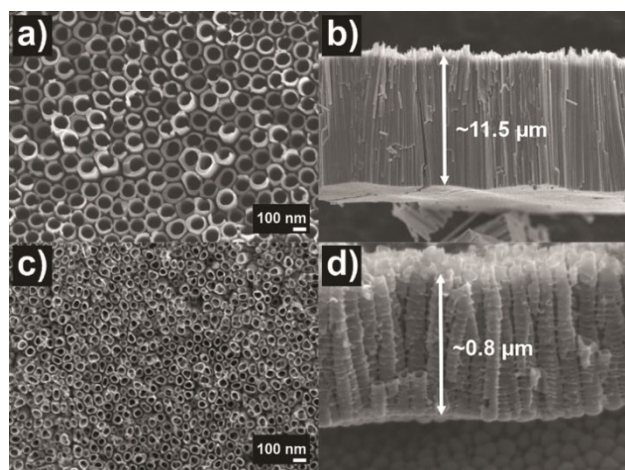

Figure 5. SEM a, c) top view and b,d) cross section images of TNT layers obtained in a closed bipolar cell on both side of the Ti substrate using alternating potential of a frequency of 5.6×10^{-4} Hz (changing the potential direction every 30 min) with an amplitude of $+60$ V in half cell 1 (a, b) and -20 V in half cell 2 (c, d). In half-cell 1 was EG-based electrolyte and in half-cell 2 glycerol-based electrolyte was used.

Rationally, also different potentials can be applied to the two half-cells. Figure 4 shows SEM images of the TNT layers obtained when potentials of $+80$ V and -40 V were applied with a frequency of 5.5×10^{-4} Hz (meaning the potential was changed every 30 min) for 6 h in total. The EG-based electrolyte was used in both half-cells. As the anodization potential is known to influence the TNT diameter and the layer thickness significantly,[4,8] TNT layers with different dimensions were obtained on the two sides of the Ti foil.

To demonstrate the versatility of this bipolar anodization approach different electrolytes were used in both half-cells. One half-cell was filled with EG-based electrolyte, the other half-cell was filled with a glycerol-based electrolyte containing 270 mM NH$_4$F and 50 vol% H$_2$O[40] (glycerol-based electrolyte). Figure 5 shows the application of potentials of $+60$ V (for the half-cell with EG-based electrolyte) and -20 V (for the half-cell with glycerol-based electrolyte) with a frequency of 5.5×10^{-4} Hz (i.e. the potential was changed every 30 min) for 6 h in total. As can be seen, the TNT layers obtained on the different sides of the Ti foil resemble TNT layers obtained in these different electrolytes in conventional anodization cells at 60 V and 20 V, respectively. This shows that the use of closed bipolar cells for the anodization of Ti substrates can be employed to produce TNT layers with completely different dimensions on both sides of the Ti substrate without the need of isolating one side. This can be interesting for applications in which different TNT layers on one substrate are needed.

To summarize, the use of closed bipolar cells for the anodization of Ti substrates towards TNT layers was shown for the first time. By applying a direct potential, the Ti substrate can be anodized on just one side, similar as in a conventional anodization cell. However, the use of an alternating potential can lead to TNT layers on both sides of the Ti substrate, with identical dimensions on both sides when alternating potentials of the same amplitude are applied. On the other hand, if potentials of different amplitude are applied and/or different electrolytes are used in both half-cells, TNT layers with completely different dimensions can be formed on both sides of the Ti substrate. Furthermore, if alternating potentials are applied, then strongly reduced TNT layers can be synthesized on the side being reduced during the last anodization cycle. The herein presented approach paves a way to successfully prepare TNT layers on previously non-anodizable substrates.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

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