

# Memristor fabrication and characterization based on TiO<sub>2</sub>

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## ABSTRACT

This work presents the development of anodic oxidation processes aimed at producing oxides with memristive behavior on valve metals. Anodic oxidation induces the growth of oxides on the surface of metals, with thickness, color, morphology and functional properties that depend on the process parameters imposed. Although many research works propose the use of anodic oxides in different fields, from corrosion resistance to wastewater advanced oxidation processes, much work is still needed to further expand engineered applications of nanostructured TiO<sub>2</sub> films, such as in the most recent field of memristive devices, where a precise control of oxide thickness and its electrical properties is required.

Here we present a study on the memristive properties of anodic oxides produced on titanium and other valve metals, in particular niobium and tantalum. Titanium was anodized in diluted sulfuric acid and phosphoric acid electrolytes, with cell voltage ranging from 0 to 100 V, and its memristive behavior was evaluated; then suitable anodizing conditions were also applied to niobium and tantalum to compare the behavior of oxides with same morphology and structure but different chemistry.

**Keywords:** anodizing, memristor, spectrophotometry, titanium dioxide, valve metal

## 1 INTRODUCTION

Today, Si - based flash memory devices represent the most prominent nonvolatile data memory (NVM) because of their high density and low fabrication costs. However, flash memory devices suffers from low endurance, low write speed, and high voltages required for the write operations. In addition, further scaling, i.e., additional increase in the density of flash memory devices is expected to run into physical limits in the near future. To overcome the problems of current NVM concepts, a variety of alternative memory concepts is explored. Most notably, NVMs based on electrically switching resistance have

attracted considerable attention, often summarized under the umbrella term resistance (switching) random access memory (RRAM) [1]. The research activity here presented deals with a particularly interesting class of RRAM in which redox reactions and nano-ionic transport processes play the key role, i.e., memristive devices.

The existence of memristors was first theorized by professor Leon O. Chua in 1971 [2], but only in 2008 researchers of Hewlett-Packard laboratories succeeded in observing a memristive characteristic in a metal/oxide/metal device built with Pt and TiO<sub>2</sub> [3]. The principle underlying TiO<sub>2</sub> memristive effects is based on the presence of oxygen vacancies moving forward and backward of the electronic barrier at the metal/oxide interface, generally through the formation of an oxygen vacancy filament, which result in the decrease in oxide resistance [4].

Here we present the fabrication of metal oxides based memristors involving the electrochemical anodization of titanium, niobium and tantalum [REF CNANO]. Anodic oxidation can be a very effective technique in the controlled production of oxide films on valve metals, tuning growth kinetics and oxide properties as a function of process parameters: in fact, it is possible to relate the controlling electrochemical parameters (cell voltage, chemical composition of the electrolytic solution, process time) to the thickness, morphology, chemical and structural composition of the growing oxide layer [6,7].

This is an inexpensive, room temperature alternative to the current methods of fabrication based on chemical or physical vapor deposition techniques, which has already proved to be suitable for the production of memristive titanium dioxide elements [8,9].

## 2 EXPERIMENTAL

Titanium specimens (grade 2 ASTM) were anodized in two different electrolytes: sulfuric acid (0.5 M) and phosphoric acid (0.5 M), with cell voltage ranging from 0 to 100 V, paying particular attention to oxides produced at low voltage (25 V and 30 V). All tests were performed at room temperature (approx. 25°C). Prior to anodizing, specimens

were degreased with acetone and either subjected to a weak acid pickling, or to mechanical polishing with multiple steps of abrasive papers down to 1200 grit, to remove possible contaminations from the metal surface. Cell voltage was measured as anode-to-cathode potential, being the anode the sample to be anodized and the cathode an activated titanium net. A current density of 10 mA/cm<sup>2</sup> was applied.

At the end of the anodizing process, the surface reflectance spectrum was measured by means of a portable reflectance spectrophotometer operating in the range 360 nm – 740 nm. Interference spectra produced by transparent thin films present a sinusoidal trend, due to interference phenomena generated at the metal-oxide-air interface due to the presence of the thin transparent oxide layer. Peaks and valleys are associated to wavelengths where a constructive or disruptive interference occurs, respectively: the position of these peaks and valleys can be translated into the oxide thickness, as described in Ref. [6].

Cyclic voltammetry was employed to record the current-voltage response of the material. The experimental setup was built with PVC to ensure complete electrical insulation. A vertical rod with copper tip (2 mm diameter) was employed as counterelectrode, allowing for rod vertical motion to correctly position the sample underneath and put the rod tip in direct contact with the oxide layer whose properties needed to be analyzed; the working electrode was connected directly to the titanium substrate. The working electrode potential is ramped linearly versus time from 0 V to  $V_f$ , with  $0.5 \text{ V} < V_f < 1 \text{ V}$ , then ramped in the opposite direction to the specular negative potential  $-V_f$ , with  $-1 \text{ V} < -V_f < -0.5 \text{ V}$ , and finally ramped back to the initial potential of 0 V. Unless otherwise stated, scan rate was set to 4 V/min.

After an optimization of anodic oxidation parameters to provide relevant memristive response was achieved on titanium, the same parameters were employed to anodize niobium and tantalum, in order to compare the memristive behavior of oxides with similar morphology and structure and different composition.

### 3 RESULTS AND DISCUSSION

#### 3.1 Titanium anodizing

Figure 1 reports anodizing kinetics, in terms of voltage increase in time, while in Figure 2 oxide thickness, calculated from reflectance spectra, is plotted as a function of the applied voltage.

Ti anodizing kinetics clearly slows down with time and with progressive oxide thickening. This effect is related to the relevant oxygen evolution taking place at the titanium surface as parasitic reaction, which decreases process efficiency. In fact, during anodizing it is possible to clearly detect oxygen bubbles forming at the metal surface in both electrolytes. In H<sub>2</sub>SO<sub>4</sub> this effect is more and more evident

at voltages higher than 70 V, which is ascribed to the concomitant onset of oxide breakdown phenomena typical of anodic spark deposition, which heat up the electrolyte and reduce process efficiency.

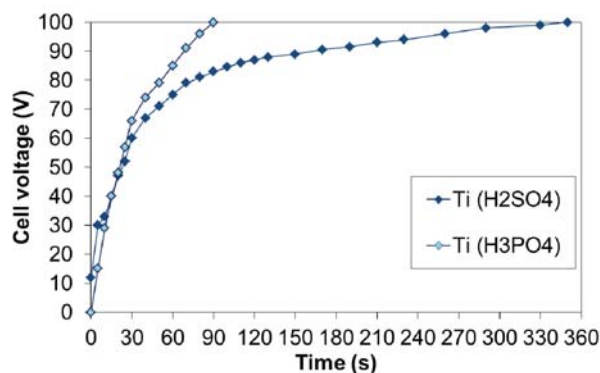


Figure 1: Anodizing kinetics recorded during titanium anodizing.

On the other hand, oxide thickness increases linearly with applied voltage, as expected; linear regression indicates an anodizing ratio of approximately 2 nm/V in both electrolytes, according with previous literature works [5]. No major difference was observed between specimens anodized in the two electrolytes.

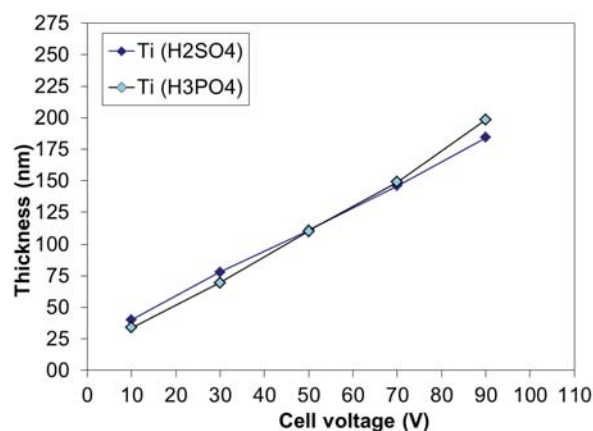


Figure 2: Oxide thickness on specimens anodized with different cell voltage and current density.

#### 3.2 Memristive behavior of anodic TiO<sub>2</sub>

A typical current-voltage characteristic response of a memristive element should present a hysteretic loop, with a high resistance state (shallow slope in I-V diagram) switching to low resistance (steep slope in I-V diagram) when overcoming a given voltage threshold, and vice versa after passing a new voltage threshold. Such a pinched loop was actually found, with loops both in the positive and negative quadrants of the I-V diagram, in most of the

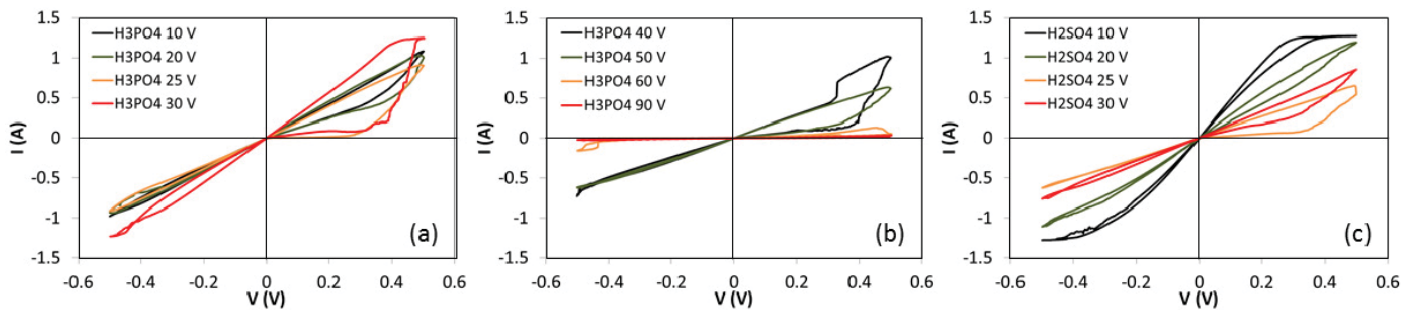


Figure 3: Cyclic voltammetry on titanium oxides obtained at different cell voltages in  $\text{H}_3\text{PO}_4$  (a and b) and  $\text{H}_2\text{SO}_4$  (c).

anodic oxides produced; yet, shape regularity and symmetry, and ratio between high and low resistance states ( $R_{\text{off}}$  and  $R_{\text{on}}$ , respectively), are the ruling parameters to identify reliable memristive switching. Therefore, several anodizing parameters were varied to test oxides with different thickness, composition and structure, and to identify optimal anodizing conditions: the comparison was based on the shape of the hysteretic loop and on the  $R_{\text{off}}/R_{\text{on}}$  parameter.

The variation of cell voltage applied during anodizing was first considered as relevant parameter to identify potentially memristive oxides. In Figure 3a and 3b cyclic voltammetry results obtained on samples anodized in  $\text{H}_3\text{PO}_4$  are reported. Samples oxidized at low voltages (10 V to 30 V) appear to be the most promising. Loops are more open in the positive quadrant compared with oxides produced at higher voltages; moreover, general results are far better than the corresponding samples anodized in  $\text{H}_2\text{SO}_4$ , reported in Figure 3c (only low voltages are shown). Taking as example the sample anodized at 25 V,  $R_{\text{off}}$  was evaluated to be  $16.92 \, \Omega$ , while  $R_{\text{on}}$  was  $0.51 \, \Omega$ , with an overall ratio higher than 30, which is already significative for a good memristive element. On the contrary, best results obtained with oxides produced in  $\text{H}_2\text{SO}_4$  did not exceed a  $R_{\text{off}}/R_{\text{on}}$  ratio of 6. At higher voltages, above 50 V, some irregularities were detected in I-V characteristics, excluding these anodizing conditions from further analyses. The reason for such behavior should be identified in the increased oxide thickness, which reaches hundreds of nanometers: in fact, memristive properties decay with increasing oxide thickness, as it hinders the formation of a through-thickness conductive channel.

On the other hand, thinner oxides did not show any memristive behavior as well: this was ascribed to opposite considerations. In fact anodic oxides generally grow as a compact film above a given voltage threshold, but in the first moments of oxide growth (typically below 10 V) such oxides may present conductive behavior, owing to an island growth model which leaves parts of the metal surface still exposed to the environment [9]. As a consequence, the high conductivity of the metal covers any possible memristive response of oxide islands.

Tests were repeated on samples that were first mechanically polished, in order to have a more homogeneous surface preparation (Figure 5). The sample demonstrated a high degree of symmetry with respect to the origin and high  $R_{\text{off}}/R_{\text{on}}$  ratio. Deviations from symmetry may be ascribed to oxide defects that play a role in trapping oxygen vacancies motion through the oxide.

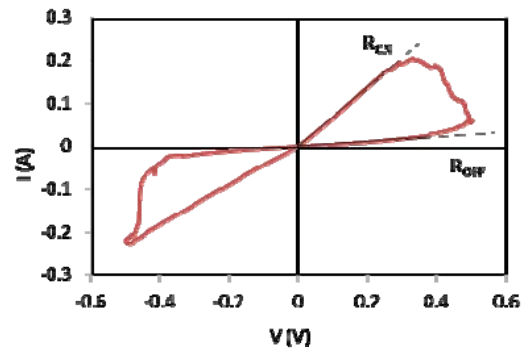


Figure 4: Cyclic voltammetry on mechanically polished titanium oxides prepared by anodizing in  $\text{H}_3\text{PO}_4$  at 30 V.

Tests were also performed at different scan rates, obtained by reducing the time required for a full scan from 30 s (corresponding to  $0.067 \, \text{V/s}$ ) to 5 s ( $0.4 \, \text{V/s}$ ). Increasing the scan rate in cyclic voltammetry caused a decrease in the opening of the hysteresis loop, reducing the  $R_{\text{off}}/R_{\text{on}}$  ratio, but still producing a significant memristive effect (Figure 5). Exceedingly high scan rates led to the almost complete closure of the hysteresis loop. Slower scan rates may facilitate the migration of oxygen vacancies, which create conducting auto-doped phases  $\text{TiO}_{2-x}$  for  $x > 1.5$ . Whereas, with a faster scan rate, the voltage increases so fast that the filament of oxygen vacancies builds up abruptly, and a steeper resistive switching is observed.

On the basis of the reported results, an optimized anodizing procedure was defined, consisting of subjecting the metal to a mechanical polishing step followed by anodic oxidation in  $\text{H}_3\text{PO}_4$  at 25 V or 30 V.

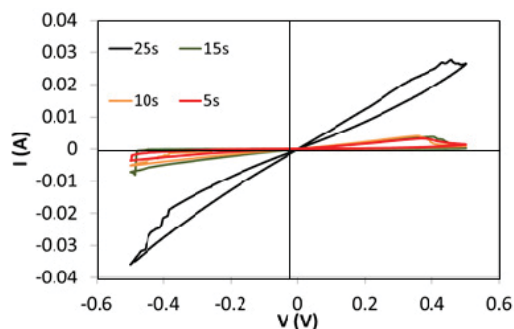


Figure 5: Cyclic voltammetry with different scan rates on mechanically polished titanium oxides prepared by anodizing in  $\text{H}_3\text{PO}_4$  at 30 V.

Further studies were also performed on niobium and on tantalum, in order to evidence possible memristive behaviors on other valve metals (Figure 6). The optimized anodizing procedure was therefore applied to both metals, and cyclic voltammetry was repeated in order to record I-V curves.

In particular, anodized niobium exhibited interesting results, with performances similar to those of anodic  $\text{TiO}_2$  combined with higher reproducibility of the experimental results.

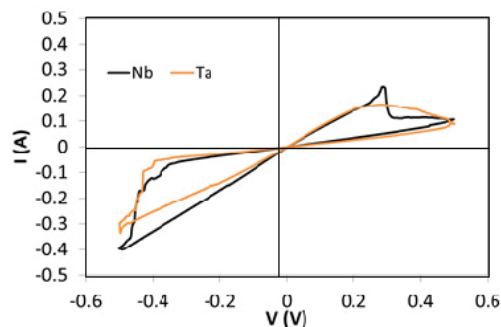


Figure 6: Cyclic voltammetry on mechanically polished niobium and tantalum oxides prepared by anodizing in  $\text{H}_3\text{PO}_4$  at 30 V.

The precise switching mechanism could not be identified, given the wide range of oxide features introduced with the different anodic oxidation parameters, including substrate composition – and consequently, oxide composition – as well as extent of surface coverage, possible presence of crystalline phases and incorporation of electrolyte ions which would modify the oxide stoichiometry. In general, performing a cyclic voltammetry produces a stressed situation in the oxide, owing to the voltage applied. It is possible to consider that the voltage stress applied during cyclic voltammetry drives oxygen ions movement: when the oxide has homogeneous  $\text{TiO}_{2-x}$  composition with  $x$  close to zero, the oxide presents high resistance, while the movement of oxygen ions towards the electrodes generates an accumulation of oxygen vacancies

that reduces oxide resistance. The whole process can be generalized as a redox process occurring at interfacial regions, which falls in the category of interfacial resistive switching.

## 4 CONCLUSIONS

The work presented investigated the possibility of obtaining anodic oxides exhibiting memristive behavior on valve metals (titanium, niobium, tantalum). Oxide thickness was observed to play a major role, being few tens of nanometers the desirable oxide thickness in order to ensure complete coverage of the metallic substrate, while avoiding exceedingly insulating thick layers. Also substrate composition concurred to the achievement of highly memristive oxides, since only anodic  $\text{Nb}_2\text{O}_5$  and  $\text{TiO}_2$  actually showed interesting switching properties, while  $\text{Ta}_2\text{O}_5$  response was far from being reproducible. This analysis still requires further implementations, and in particular the role of the top electrode, which was neglected in this initial evaluation, should be taken into account as it can strongly affect the oxide behavior.

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