



## Electrochemical surface modification of titanium in Chemistry Class

Philipp Lanfermann<sup>1</sup>, Christoph Weidmann<sup>1</sup>, Mona Christin Maaß<sup>1</sup>, Stefanie Waitz<sup>1</sup>, Tina Schönberger<sup>1</sup>, Thomas Waitz<sup>1</sup>

Department of Chemistry Education, Georg-August-Universität Göttingen, Germany<sup>1</sup>

### Abstract

Surface modification techniques play an important role in materials science and engineering. The anodic oxidation of aluminum is a well-known example to demonstrate the improved corrosion resistance [1] and is therefore used in science classes regularly. The same process can also be applied to titanium with the benefit that the oxide layers cause an intense coloring due to interference effects [2,3]. This can be used in classes to establish a simple correlation between the observed color and the thickness of the oxide layer. Herein, we present simple electrochemical experiments for the synthesis and characterization of titanium dioxide layers for educational purposes. They can be obtained by a facile setup using commercially available titanium sheets and a mildly acidic aqueous electrolyte within seconds or minutes. By varying the synthesis parameters (e.g. voltage, electrolyte, reaction time), morphology and thickness of these layers can be controlled. In our contribution, we explain the relation between observed color and thickness using a simple model. Further aspects will cover educational experiments using digital data logging and characterization methods like scanning electron microscopy. Furthermore, the industrial relevance of titanium surface modification for improved properties like corrosion resistance and electrical conductivity is shown.

**Keywords:** surface modification, anodic oxidation, interference

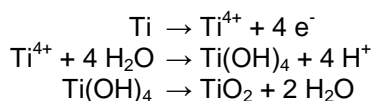
### 1. Introduction

The control of surface properties is a field of intensive research and development in materials science. The central goal is to improve or extend the functionality of materials by specifically adapting properties such as adhesion, conductivity, hardness, friction, and biocompatibility or corrosion resistance through physical or chemical modifications. In recent decades, various techniques have been developed and established for this purpose, for example in the field of sol-gel chemistry or electrochemistry. However, the topic of surface modification is already part of chemistry classes, for example in the context of the fabrication of hydrophobic and hydrophilic glasses or the electrochemical oxidation of aluminum surfaces by means of the 'anodizing process' (Eloxal-Process) [4,5].

In the present contribution we tie in with electrochemical methods and present an approach for the generation of colored layers on so-called valve metals (titanium, zirconium, and hafnium) using the example of the production of TiO<sub>2</sub>. By varying the reaction parameters, in particular the applied voltage, it is easily possible to produce differently colored layers on titanium sheets, which not only have an aesthetic appearance but also possess an improved resistance to chemicals for example. Furthermore, we present models and schematic drawings suited for K12 chemistry class, which should help to understand the underlying chemical processes during the fabrication of these layers as well as their different colors caused by interference phenomenon.

### 2. Background

The titanium dioxide layers are produced in the experiments presented using an anodic oxidation process. For this purpose, a DC voltage is applied to two titanium electrodes in an electrolyte of weakly concentrated oxalic acid. While hydrogen gas is produced on the cathode side, a layer of TiO<sub>2</sub> is formed on the titanium electrode acting as anode.



After the initial formation of a thin TiO<sub>2</sub> layer, there is no direct contact between the metal surface and the electrolyte. The growth in thickness can therefore only take place when mobile species (in this case Ti<sup>4+</sup> and O<sup>2-</sup>) can be transferred through the oxide barrier which is described in literature (see fig. 1 [6]). On the Ti/TiO<sub>2</sub> interface, Ti(IV) species are generated by anodic oxidation which are transported



to the  $\text{TiO}_2$ /electrolyte interface to form a  $\text{TiO}_2$  layer while  $\text{O}^{2-}$  moves towards the Ti anode. The transport of these charge carriers is driven by the electric field although the ionic conductivity of  $\text{TiO}_2$  is fairly small. The observed current and therefore the reaction rate is continuously decreasing as the layer grows in thickness, eventually reaching a stable oxide layer with no further growth. This explains why much higher potentials are needed to form a substantial oxide layer than one would expect when taking the redox potential of  $\text{Ti(IV)/Ti}$  (e.g.  $E_0 = -0.88 \text{ V}$  for  $\text{Ti/Ti(OH)}_2^{2+}$  [7]) into account.

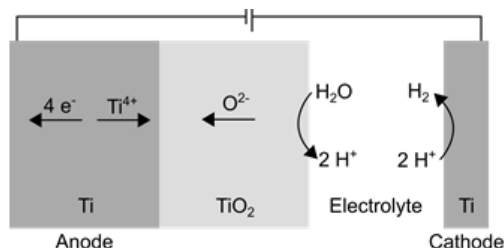


Figure 1: Schematic representation of the reactions during oxide layer growth (adapted from BERGER) [6].

The corresponding thickness of this oxide layer is determined by the voltage used to drive the charge carrier movement rather than the reaction time and can therefore be controlled using this parameter. The obtained layer thickness of 50 - 150 nm results in interference effects with visible light producing color impressions precisely controllable by the anodization voltage [2]: Incoming light is partially reflected directly by the oxide layer. However, some light travels through the transparent oxide layer and is reflected at the titanium metal. This light travels an additional distance compared to the light that is reflected by the oxide layer. Thus, there is a path difference between the two light beams. The overlap of both rays after reflection therefore leads to interference effects. The visible color represents the complementary color of the wavelength range that was cancelled out by destructive interference.

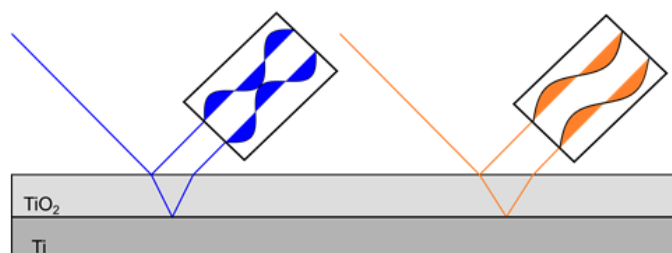


Figure 2: Representation of destructive and constructive interference.

### 3. Experimental

#### 3.1 Preparation of colored titanium sheets by anodic oxidation

Titanium dioxide layers with different color impressions are produced by anodic oxidation in a simple two-electrode setup.

**Equipment:** voltage source, cable, crocodile clips, beaker (200 mL), resistance meter, stand material.

**Chemicals:** oxalic acid (4 % in water), titanium sheets, distilled water.

**Procedure:** Anodic oxidation is carried out at voltages of 5 - 65 V in 10 V steps, with the titanium sheets acting as the electrodes and the oxalic acid solution as the electrolyte. After the samples have been anodized for one minute, the titanium sheet acting as the anode is rinsed with distilled water and replaced by a new sheet. Subsequently, the electrical resistance of an untreated and the sheet anodized at 65 V is measured. Due to possible damaging of the oxide and thus erroneous measurements, care should be taken to apply as little force as possible.

**Observations:** Figure 3 shows the anodized titanium sheets displaying a broad range of colors. While the untreated titanium shows a very low resistance (several  $\text{m}\Omega$ ), the anodized sheet displays a resistance in the  $\text{M}\Omega$  range.

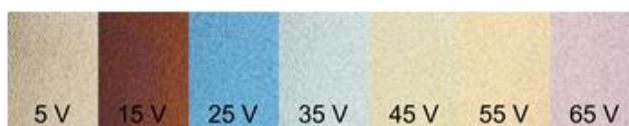


Figure 3: Color of titanium sheets anodized at different voltages.



**Interpretations:** A layer of titanium dioxide is formed on the anode, the thickness of which correlates with the level of applied voltage.  $\text{TiO}_2$  is an electrically non-conductive material, accordingly the measured electrical resistance of the anodized titanium is very high. Due to the interference effects on thin layers, the sheets show a distinct color depending on the thickness of the oxide layer extinguishing the complementary color by destructive interference (see fig. 4). This color associated with the applied voltage confirms the correlation of layer thickness and the voltage used to drive the charge carrier movement.

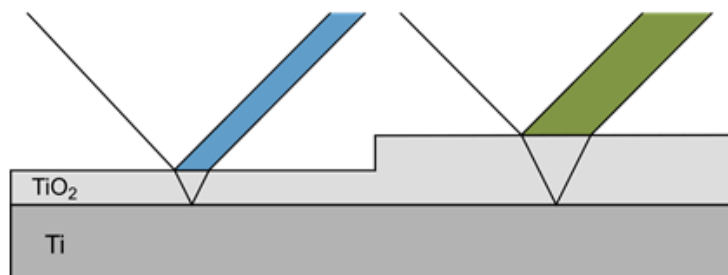


Figure 4: Effect of oxide layer thickness on the visible color upon irradiation with white light.

### 3.2 Two-step anodization

A two-step anodization process is used to confirm the voltage-color-relation and to show potential applications for aesthetic purposes.

**Equipment:** voltage source, cable, crocodile clips, beaker (200 mL), stand material, digital current measurement device (PHYWE Cobra SMARTsense connected to a tablet computer).

**Chemicals:** oxalic acid (4 % in water), titanium sheets.

**Procedure:** Electrolysis is performed as in 3.1 at 15 V and 35 V and the currents are recorded using digital measurement data acquisition. Afterwards, the titanium sheet anodized at 15 V will be placed back in the electrolyte and anodized at 35 V and the current is recorded again.

**Observations:** It can be observed that the current drops to almost 0 A after only a few seconds (see fig. 5). As expected, the titanium sheets anodized at 15 V and 35 V show different interference colors but after the second step at 35 V, they appear virtually identical (see fig. 5).

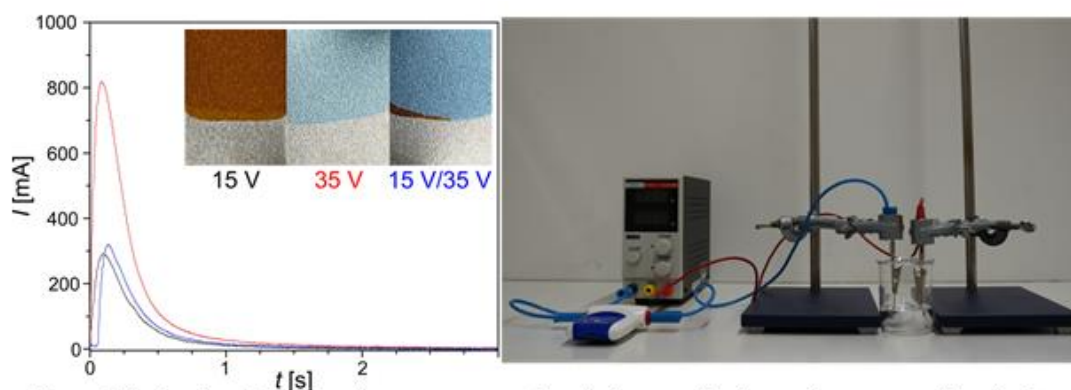


Figure 5: Left: plot of measured current versus time during anodization and corresponding titanium sheets. Right: experimental setup.

**Interpretations:** As long as a significant current flows, titanium dioxide is formed and the layer grows. After a few seconds, the layer reaches a thickness where the electrical field is no longer able to ensure ion conduction within the oxide. Due to the electronically insulation property of the oxide layer, which was shown by measuring the resistance in 3.1, no further reaction such as the electrolysis of water can take place and thus no current can flow. With increasing voltage, the oxide growth continues, confirming that the layer thickness is determined by the applied voltage and allows further experiments: A coating before the second anodization step and its subsequent removal can be used to draw colored pictures or symbols (see fig. 6).



Figure 6: Different pictures obtained using a two-step anodization process.

### 3.3 Increasing the corrosion resistance by anodic oxidation

Contact with hot hydrochloric acid demonstrates the improved corrosion resistance of the anodized titanium.

**Equipment:** hot plate, stirring bar, beaker (200 mL), stand material.

**Chemicals:** untreated titanium sheet, anodized titanium sheet (anodized at 60 V), concentrated hydrochloric acid, distilled water.

**Procedure:** Half of both titanium sheets are suspended in hot (approx. 80 °C) concentrated hydrochloric acid. After 15 minutes, the sheets are removed from the solution, washed with distilled water and dried.

**Observations:** The anodized sheet remains largely unchanged despite prolonged contact with the hydrochloric acid. The untreated sheet, on the other hand, is clearly discolored and corroded (see fig. 7).

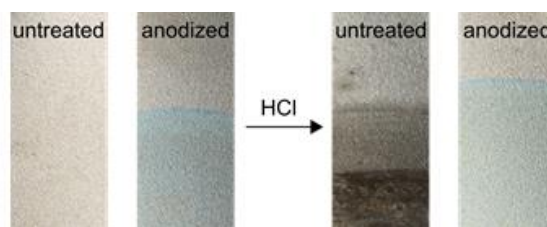


Figure 7: Untreated and anodized titanium before and after contact with concentrated hydrochloric acid.

**Interpretations:** The untreated titanium surface is susceptible to hot concentrated hydrochloric acid and corrodes quickly. Even though there is a thin oxide layer on the titanium surface due to oxidation in air, it is not sufficient to protect the titanium from the influence of the acid [7]. The layer formed by anodizing, on the other hand, is significantly thicker than the naturally occurring one and can withstand the contact with the hydrochloric acid without any visible influence on the oxide layer and the metal beneath.

## 4. Educational considerations

The anodic oxidation of titanium is a suitable topic for chemistry classes to combine basic electrochemical processes, physical phenomena like interference and industrial applications for surface modification in visually striking experiments. On the one hand, they are already familiar with products resulting from the same manufacturing method in their everyday lives. For example, titanium jewelry, spectacle frames and many items are colored in this way. In addition, they have encountered the phenomenon of interference on thin layers: The colorful effect of soap bubbles and oil traces is based on this mechanism.

The formation of titanium dioxide layers can be integrated into the context of electrochemistry. The basis for layer formation is a facile electrolysis. Accordingly, in addition to basic knowledge of redox reactions, the students should be familiar with the separation of anodic and cathodic reactions in an electrolytic cell. Additionally, the practical requirements can be easily met in schools, since only titanium sheets, oxalic acid and common voltage sources are needed. The short reaction times allow for the fabrication of a wide range of colored titanium sheets, making the experiment visually appealing.

Furthermore, the discussed relation between color, layer thickness and voltage enables the students to determine the anodization voltage used for the production of colored titanium goods in everyday life. A possible drawback could be the voltage sources used in schools, which often cannot reach voltages of up to 60 V. Instead, it can be decided to use only low voltages, since even between 5 - 15 V distinctly colored layers are created. Alternatively, several voltage sources can be connected in series, where local regulations for science classes should be considered.

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