


## Coloring of a Titanium Plate as an Experimental Teaching Material for Demonstration during Introduction to Electrochemistry

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### Abstract

Coloring of a titanium plate on an experimental scale by means of an electrochemical reaction is proposed, and the plate is used as a teaching material for demonstration during introduction to electrochemistry. The plate was readily colored, and variable sequential changes in the color pattern could be observed and controlled by adjusting the experimental conditions such as anodizing voltage and anodizing time. For example, sequential color changes from the original gray to blue, cyan, and then to green was observed under applied voltages of 20 to 30 V.

**Keywords:** Titanium coloring, Demonstration, Experimental teaching material, Electrode oxidizing

### Introduction

A fundamental feature of school lessons in science and chemistry has been introduced, in which a Special Emphasis on Imagination is regarded toward Creation (SEIC) based on a Special Emphasis on Imagination to Creation (SEIC) [1, 2]. Promoting creativity in science teaching has been discussed in the literature [3-7]. It is important for students to think imaginatively and act accordingly, in order to have an outcome that is of value to the original objective [8, 9]. This helps the students realize and understand phenomena related to chemical education.

Visualization of phenomena can help to further one's ability to understand abstract concepts in chemistry. It is no exaggeration to say that visual teaching materials in chemical education, such as interesting experiments, instruments, videos, and CG graphics, are very important. The visual methods need to be user-friendly and appealing to students from the standpoint of a useful teaching material.

Titanium is an interesting material in chemistry and science education as well as for

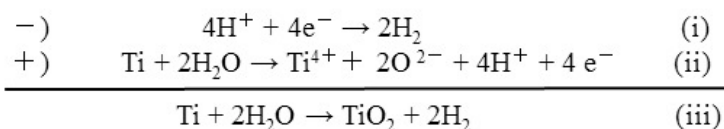
practical application in science and technology, *e.g.*, coloring titanium objects for decorative purposes, titanium alloy utilization in hydrogen storage, and so on. Titanium can be colored in a variety of vivid shades and used in industry as for aesthetic purposes. Titanium coloring by anodic oxidation [10, 11] and the use of titanium alloy as a counter electrode [12, 13] have been reported. Normally, colored titanium plates are manufactured on a large scale under a high anodizing voltage for example, by soaking a titanium plate in a solution of 1.5M H<sub>2</sub>SO<sub>4</sub> and 0.3M H<sub>2</sub>O<sub>2</sub> under an applied voltage of 200 V and direct current density of 3.0 Adm<sup>-2</sup> [14].

In this work, we aimed to create a teaching material that gives students a positive experience in discovering the "how" and "why" of chemical reactions. Teaching materials that are dominated by the visual effect of a phenomenon can increase the student's interest in the lesson and thus promote understanding. This paper provides a method for coloring titanium on an experimental scale, to be used as teaching material for demonstration during the introduction to the unit of electrochemistry in chemical education.

## Experimental

### Theory of titanium coloring

The chemical reaction underlying the anodizing process is as follows:  $\text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ + 4\text{e}^-$  [15]. The reaction at each electrode proceeds as shown in Scheme 1. Anodizing involves the formation of an oxide film layer on the titanium surface, and films of various colors can be generated. The color generation is due to the interference of light waves, as per the phenomenon of Newton's rings, caused by an interference action from the reflection of light and a refraction phenomenon [16, 17]. Generally, the film thickness is directly related to anodizing voltage, such that the thickness increases with increasing voltage [18, 19]. Principles of chromaticity were introduced by an International Committee entitled CIE [20] as international standards, which were based on widely used visual experiments involving color changes over a wide range. The CIE chromaticity system is the only internationally accepted metric system for measuring color.



**Scheme 1** Electrode process

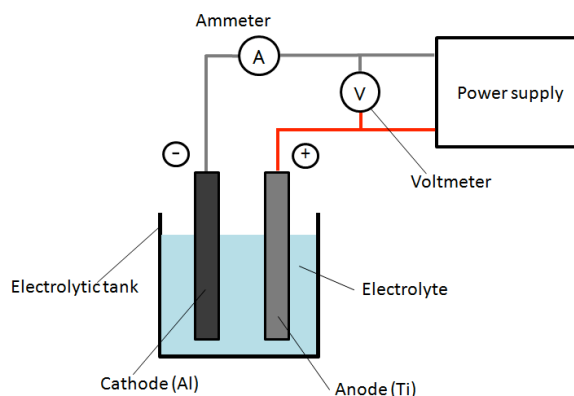
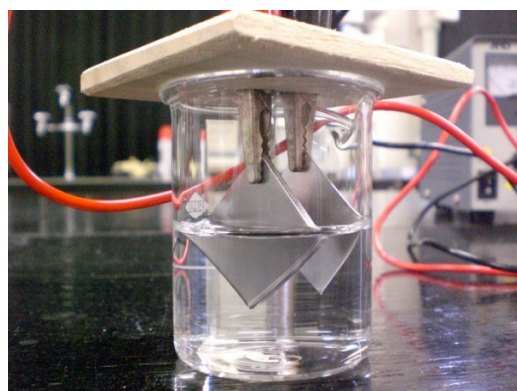
### Titanium plate and anodizing conditions

A pure titanium plate of the JIS second class grade was obtained from Sumitomo Metal Industries, Ltd. The minor chemical ingredients in the titanium plate are listed in Table 1.

**Table 1** Properties of Ti plate <sup>a)</sup>

Pure Ti (JIS second class)	Chemical components / %							
	H	O	N	Fe	Al	V	Sn	Cr
	0.002	0.082	<0.001	0.05	***	***	***	***

a) Titanium plate was purchased from Sumitomo Metal Industries, Ltd.



**Fig. 1** Electrolysis equipment

The electrode oxidizing equipment used in the anodizing process and the schematic diagram of an electric circuit are shown in Fig. 1. The electrode dimensions were 25 mm x 25 mm x 2 mm, with the titanium plate used for the anode and an aluminum plate for the cathode. The electrodes were separated by a distance of 10 mm and partly immersed in a 50 mL aqueous solution of 1.0 wt% phosphoric acid as an electrolyte, as shown in Table 2.

**Table 2** Typical experimental conditions

Ti (anode) & Al plate (cathode):	25 x 25 x 2 mm
Distance between the electrodes:	10.0 mm
Electrolyte:	1.0 wt%-Phosphoric acid aqueous solution (50 mL)
Applied voltage:	0 - 30.0 V (elevated voltage/ 10.0 Vs <sup>-1</sup> )

### Experimental procedure

A flow diagram of the experiment with titanium plate treatment is shown in Appendix 1. The titanium plate was processed by thorough polishing, mirror finishing, degreasing, and rinsing, prior to anodic oxidation treatment. Following the oxidation process, the titanium plate was rinsed and dried.

## Results and Discussion

### Color change vs. anodizing time

The color change of the titanium plate when the anodizing time was consecutively increased from 1 min to 240 min under an applied of voltage 30 V was monitored (Fig. 2).

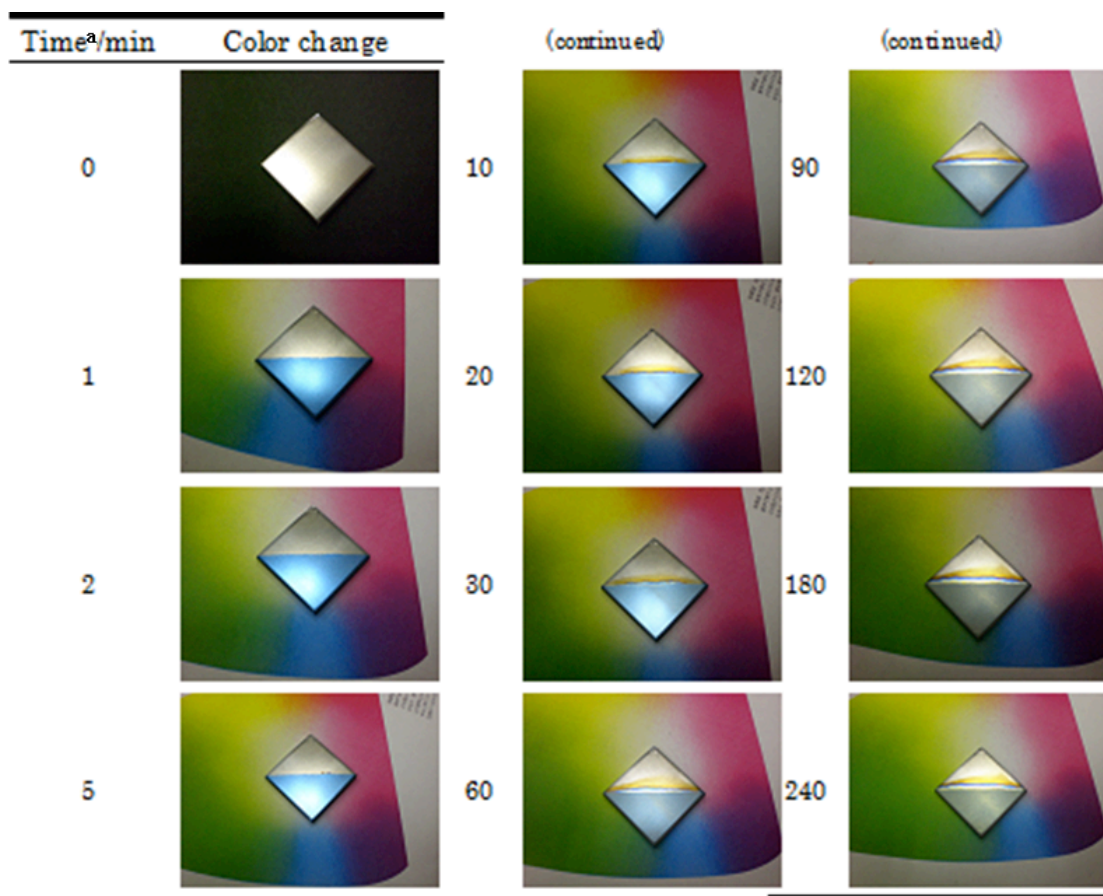


Fig. 2 Color change of Ti plate vs. anodizing time. Applied voltage: 30.0

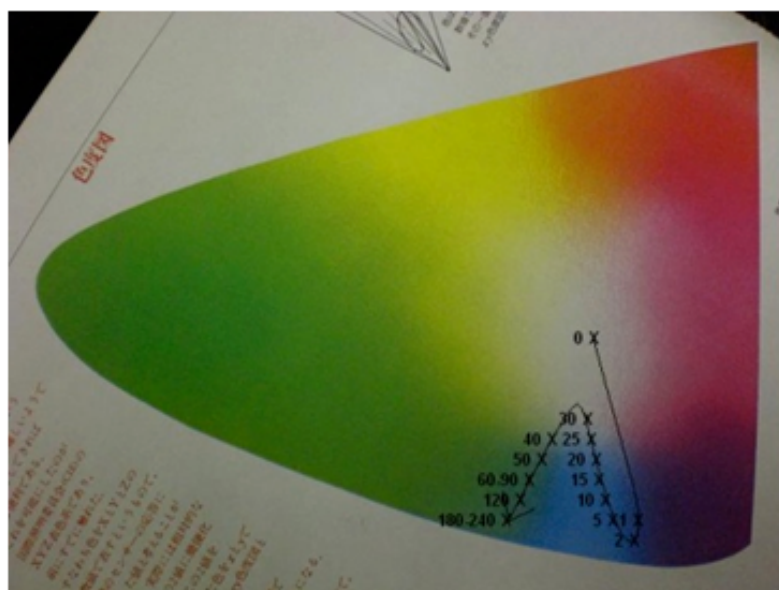


Fig. 3 Trace on CIE<sup>a</sup> chromaticity diagram.

a) CIE: Commission. Internationale de l'Éclairage [20].

A vivid color was observed in the period color was observed in the period from 1 min to approximately 30 min. A particularly vivid blue color was observed after 1 min of anodizing. After 30 min, the plate assumed a darker blue color. The colors of the titanium samples were plotted to follow the sequence of color tone change on the CIE chromaticity diagram (Fig. 3). A sequential color change was observed, and this tendency is summarized in Table 3 for an in-depth review.

**Table 3** Color change of Ti plate vs. anodizing time

Time <sup>a)</sup> /min	Color change		
	Hue	Saturation <sup>b)</sup>	Brightness <sup>c)</sup>
1	Blue	9	9
2	Blue	8	8
5	Blue	7	7
10	Cyan	6	6
20	Cyan	5	5
30	Cyan	4	4
60	Green	3	3
90	Green	2	2
120	Green	0	1
180	Green	1	0
240	Green	1	0

Anodizing voltage: 30 V. a) Anodizing time; b) Colorfulness: rating shows the relative strength of the appearance; c) Lightness: rating in the same manner as b).

The color tone, or hue, is distinguished using the six basic colors red, green, blue, cyan, magenta, and yellow. The rating values of saturation and brightness are shown as relative intensities by comparison of all samples, where the highest rating is classed as nine and the lowest as zero. With increasing anodizing time, the blue color changed initially to cyan and then to green, accompanied by a decrease in the intensity of both saturation and brightness. An anodizing time of 1 min was sufficient for obtaining high values of both saturation and brightness.



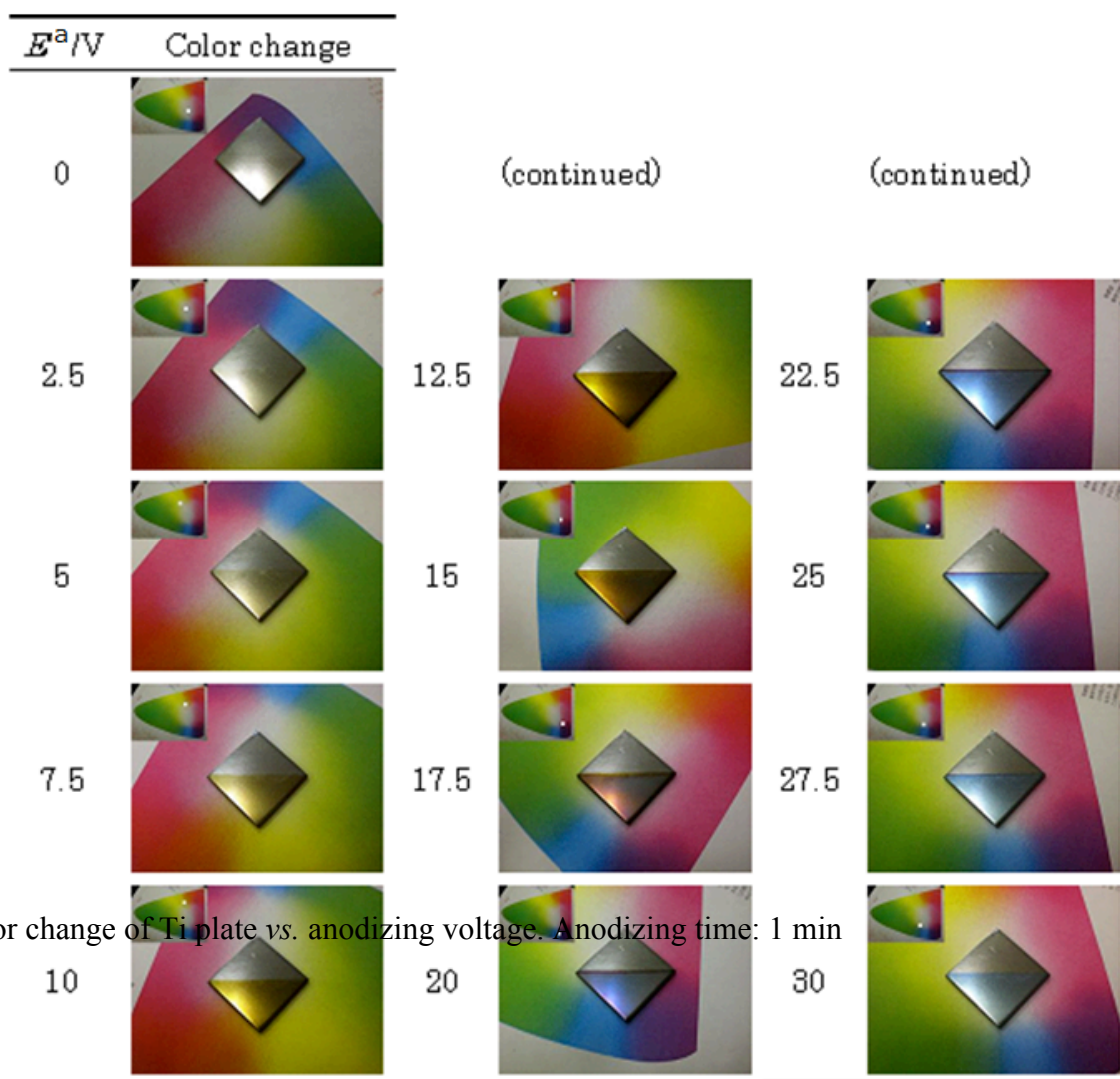


Fig. 4 Color change of Ti plate vs. anodizing voltage. Anodizing time: 1 min

#### Color change vs. anodizing voltage

The dependence of the applied anodizing voltage on titanium coloring was monitored by consecutively increasing the voltage from 0 to 30 V; an anodizing time of 1 min was used throughout this phase of experimentation. A vivid color change was observed with variation in the anodizing voltage; sequential color change progressed from yellow, to red, magenta, blue, cyan, and then to green as the voltage was increased (Fig. 4). This sequential color change is plotted on the CIE chromaticity diagram in Fig. 5. The number on the CIE diagram is the sample number corresponding to a voltage of 0 V to 240 V. The sequential color change pattern on CIE diagram in the range 20 to 30 V was similar with that in the range 1-240 min in the case of “color change vs. anodizing time” shown in Fig. 3. The trend in the color change is summarized in Table 4. The values of saturation and brightness were obtained as

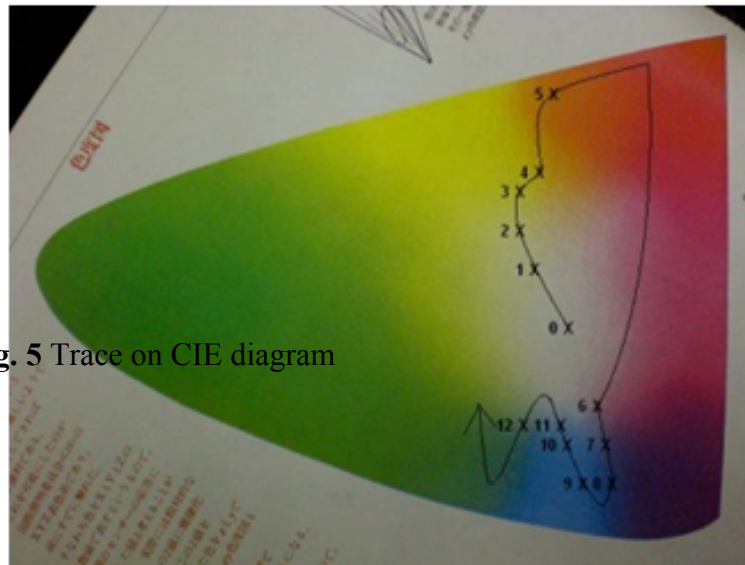


Fig. 5 Trace on CIE diagram

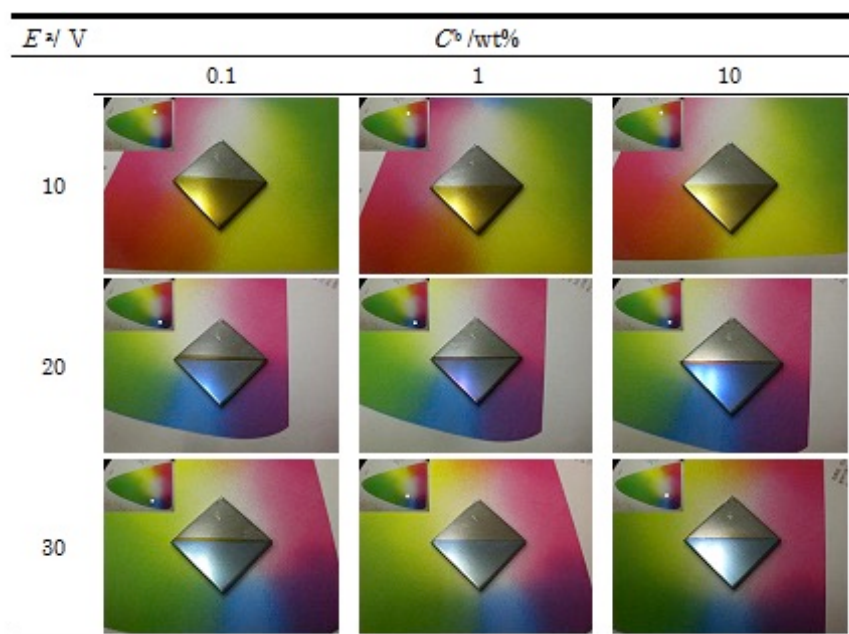
$E^{*d})/ V$	Color change		
	Hue	Saturation <sup>b)</sup>	Brightness <sup>c)</sup>
0	Clear	0	9
2.5	Yellow	1	8
5	Yellow	2	7
7.5	Yellow	3	6
10	Yellow	8	6
12.5	Yellow	9	1
15	Red	8	0
17.5	Magenta	7	3
20	Blue	9	1
22.5	Blue	8	2
25	Cyan	6	4
27.5	Cyan	5	5
30	Green	4	6

previously described in the section “Color change vs. anodizing time.” The initial yellow color was developed upon increasing the voltage, resulting in an increase in the saturation value and a decrease in the brightness value. Changing the anodizing voltage was effective for generating titanium plates of various colors.

**Color change vs. concentration of electrolyte**

The dependence of phosphoric acid (electrolyte) concentration on titanium coloring was investigated at anodizing voltages of 10, 20 and 30 V, for 1 min. The concentration of the electrolyte solution was compared at 0.1, 1.0, and 10.0 wt% aqueous phosphoric acid. The color changes are shown in Fig. 6. A vivid color was observed in all instances, with blue color

**Fig. 6** Color change of Ti plate vs. concentration of electrolyte (0.1 - 10.0 wt%) a) Applied voltage: 10.0 V - 30.0 V; b) Concentration of phosphoric acid aqueous solution (50 mL). The color change tendency at different concentrations of the electrolyte correlated with the change from yellow to blue mentioned in the section “Color change vs. anodizing voltage.”



**Inclusive discussion**

Normally, large-scale manufacture under a high anodizing voltage has been adopted for the production of colored titanium plates, e.g., soaking a Ti plate in a solution of -1.5M H<sub>2</sub>SO<sub>4</sub> and 0.3M H<sub>2</sub>O<sub>2</sub> under an applied voltage of 200 V and direct current density of 3.0 Adm<sup>-2</sup>



[14]. In this study, variable color changes have been observed in an electrode oxidizing process on an experimental scale, under a low applied voltage in the range 2.5 to 30.0 V. A sequential color change from yellow to red, magenta, blue, cyan, and then to green was observed as the applied voltage was increased. By comparison of the varying anodizing voltage and anodizing time experiments, the sequential color change pattern of blue, cyan, and green observed in the range 20 to 30 V when increasing the voltage (Fig. 3) was similar to that seen in the full range, 1 to 240 min, of increasing anodizing time (Fig. 5). The relation between the film thickness and the anodizing voltage has been reported [21]. The film thickness increased with an increase in applied voltage from 10 to 40 V and was accompanied by an apparent color change from pale brown to violet, cobalt, and then to pale blue. A similar result has been reported with apparent color change from gold to brown, and then to blue with the film thickness ranging from 0 nm to 50 nm, where the applied voltage was increased from 0 to 40 V [22]. However, it has been documented that film thicknesses greater 100 nm are difficult to achieve using the electrode anodizing process [23]. These reports suggest that the maximum film thickness in this work was approximately 50 nm at voltages of 20 to 30 V, and a thinner film was generated in the lower voltage range, 2.5 to 17.5 V, with color change to yellow, red, and magenta. This sequentially vivid color change should help in promoting a student's interest in electrochemistry.

### Conclusion

Coloring of a titanium plate on an experimental scale has been demonstrated by means of an electrochemical reaction. I believe that this phenomenon in which sequential treatment results in vivid variations in color such as yellow, red, magenta, blue, cyan, and green will motivate students to study chemistry. These color variations can be achieved by varying the anodizing time, anodizing voltage, and the concentration of phosphoric acid in the electrolyte solution. With reference to previous studies found in the literature, the film thickness was inferred from the color change to be in the range from 0 to 50 nm. Coloring of a titanium plate on an experimental scale can be adopted as teaching material for an experimental demonstration when introducing the field of electrochemistry.

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## Appendix 1

<b>Ti plate (25 mm × 25 mm × 2 mm)</b>
<b>Polishing · Mirror finish</b> i) Abrasives for copper & brass ii) Silver polishing Cloth
<b>Degreasing · Rinsing</b> i) Immersion [6M·NaOH (20 mL), 1 min] ii) Rinsing [Water (100 mL)] iii) Wipe off [95 v/v% Ethanol] iv) Rinsing [Detergent, Water (500 mL)] v) Wipe · Dry
<b>Anodic oxidation</b> [1 wt% phosphoric acid] Constant voltage condition
<b>Rinsing · Dry</b> [Water (500 mL)] & Cotton fabric
<b>Oxide filmed Ti plate (coloring Ti plate)</b>