

# Activation of passivated titanium anodes from the electrolysis of MnO<sub>2</sub>

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Titanium anodes with and without a MnO<sub>2</sub> precoat were passivated during deposition of electrolytic manganese dioxide and subsequently activated by cathodic reduction. The time dependence of the titanium voltage during passivation and during cathodic reduction was determined by the initial state of the surface. Nonactivated titanium passivated considerably faster than activated titanium with the same thickness of precoat. The application of cathodic currents to passivated anodes caused detachment of the precoat and reduction of the passivating film underneath the precoat. Reduction of the passivating film grown on precoated titanium seems to occur at a much smaller rate than reduction of the film grown on unprecoated titanium.

## 1. Introduction

Deposition of electrolytic manganese dioxide (EMD) on titanium anodes usually results in passivation of the anodes after sometime of deposition. This causes a degraded EMD product and, eventually, a halt in the EMD deposition process. The passivation is evidenced by a sudden rise in electrolytic voltage under galvanostatic deposition. Several means are known to extend the anode life by applying a coating of MnO<sub>2</sub> to titanium [1–3]. The coating layer is a very hard deposit and it is strongly attached to the substrate. To reactivate a passivated anode both the coating and the passivating film must be removed. A common procedure involves sandblasting to remove the coating layer, followed by chemical etching, to remove most of the passivating film. In this work, we show that reactivation of passivated precoated titanium can be accomplished by applying cathodic currents.

## 2. Experimental procedure

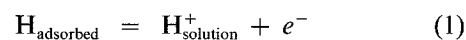
Commercially pure sandblasted titanium and graphite were used as the anode and cathode, respectively, in an electrolysis bath. The electrolyte was composed of 1 M MnSO<sub>4</sub> in 0.3 M H<sub>2</sub>SO<sub>4</sub> at 90 ± 2°C. Activated and nonactivated titanium samples were used. The activated samples were prepared galvanostatically at a cathodic current of 5 mA cm<sup>-2</sup>. The nonactivated samples were prepared by an etch for 10 s in a diluted solution of 35% HNO<sub>3</sub> and 5% HF at room temperature. To retard passivation, a thin precoat of MnO<sub>2</sub> was deposited on titanium potentiostatically. Deposition of EMD was done galvanostatically at high current densities. During EMD deposition and cathodic reduction, the titanium voltage was measured with respect to a saturated Ag/AgCl reference electrode.

## 3. Results and discussion

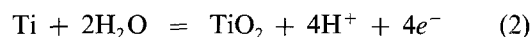
Unlike nonactivated titanium, activated titanium at

open circuit displayed a steady voltage of  $-0.8 \pm 0.05$  V and hydrogen evolution from the surface. Deposition of EMD on unprecoated titanium at current densities higher than 12 mA cm<sup>-2</sup> caused a rapid voltage rise soon after deposition started (Fig. 1). The precoat on titanium delayed the voltage rise to various times proportional to the precoating time, that is, thickness. The thicker the precoat the longer the sample stayed at a relatively low voltage, as Fig. 2 shows. In this figure, 30 min of precoating is equivalent to a precoat of approximately 1.5 μm thick, estimated from measurements done on precoats thicker than 50 μm and presuming a linear relationship between deposition time and thickness. The relationship between the time for the voltage to start rising and the precoating thickness was not direct.

During EMD deposition, nonactivated titanium passivated faster than activated titanium with the same thickness of precoat. Curves (a) and (b) of Fig. 3 show the respective voltage curves during passivation of samples with 55 μm of precoat. The time difference in voltage rise between both samples was probably caused by a difference between them in the initial oxide thickness. Prior to precoating, the oxide thickness on nonactivated titanium is thicker than that on activated titanium [4]. During precoating, the oxide on nonactivated titanium will get even thicker. The anodic potential applied to activated titanium to begin precoating is expected to first oxidize all the available unrecombined hydrogen at the titanium surface (H<sub>adsorbed</sub><sup>+</sup>) to hydrogen ions in solution (H<sub>solution</sub><sup>+</sup>) according to [5, 6]



After the available hydrogen is consumed, oxidation of titanium would begin according to [7]



Simultaneously, oxidation of Mn(II) to Mn(IV) forms

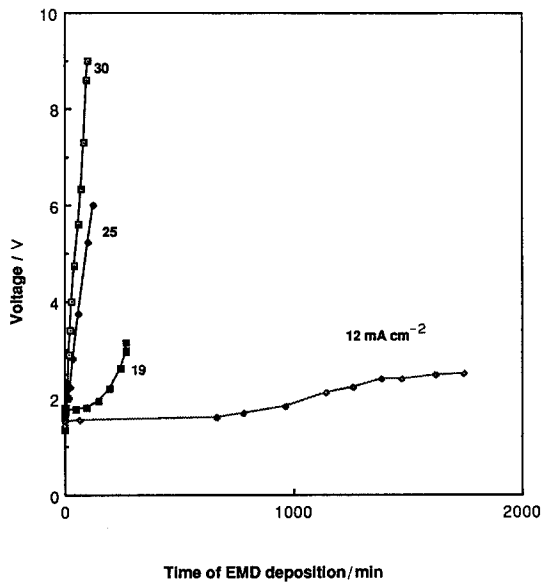


Fig. 1. Voltage of unprecoated titanium during EMD deposition at various current densities.

the precoating layer of  $\text{MnO}_2$  [8]. Growth of this layer suppresses the oxidation of titanium during precoating [9]. Unlike activated titanium, nonactivated titanium lacks excess of hydrogen at the surface [10] and would be expected to grow an oxide film as soon as the anodic potential is applied to begin precoating. As a result, a thicker oxide is present on nonactivated titanium after precoating. This would cause nonactivated samples to passivate faster than activated samples during EMD deposition.

Application of cathodic currents to passivated pre-coated titanium caused detachment of the precoating layer and reduction of the passivating film. The precoat detached from the substrate during the latter stages of the reduction process which corresponded with the evolution of hydrogen. These events started before the voltage attained a negative steady value.

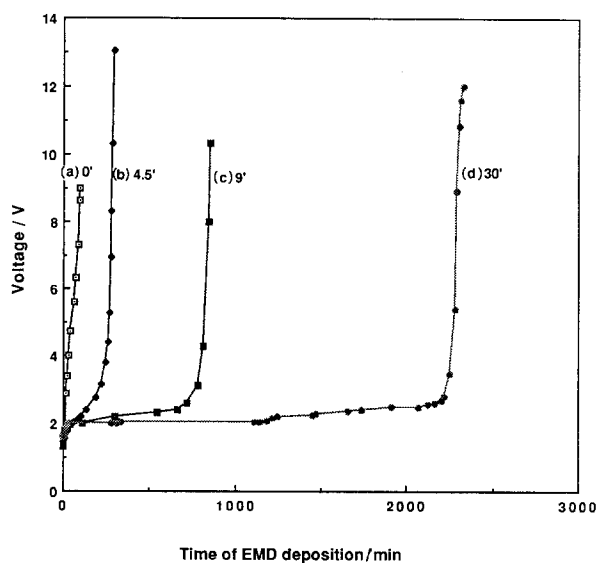


Fig. 2. Voltage of titanium samples precoated with  $\text{MnO}_2$  during EMD deposition at  $30 \text{ mA cm}^{-2}$ . The time of pre-coating on each sample is indicated in minutes.

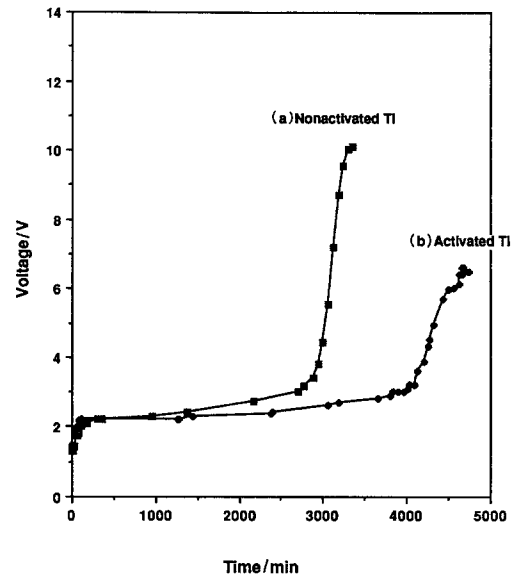


Fig. 3. Voltage of titanium precoated with  $55 \mu\text{m}$  of  $\text{MnO}_2$  during EMD deposition at  $30 \text{ mA cm}^{-2}$ . (a) Nonactivated titanium and (b) activated titanium.

The pressure exerted by the evolving hydrogen probably caused the EMD to break away from the substrate. Figure 4 shows the voltage during cathodic reduction of the sample passivated as shown in Fig. 3a. The EMD deposit was scraped before applying cathodic reduction to this pre-coated sample. The observed steady voltage value of near  $-0.8 \text{ V}$  at the end of the reduction is characteristic of titanium in the activated state. After reaching this state, the anode surface was bright and ready to be pre-coated again. Figure 5 illustrates another example of cathodic reduction applied to a titanium sample passivated during EMD deposition. The anode had initially a  $50 \mu\text{m}$  thick precoat. Two cycles of EMD deposition at  $33 \text{ mA cm}^{-2}$  followed immediately by cathodic reduction at  $-3.3 \text{ mA cm}^{-2}$  are seen. The second

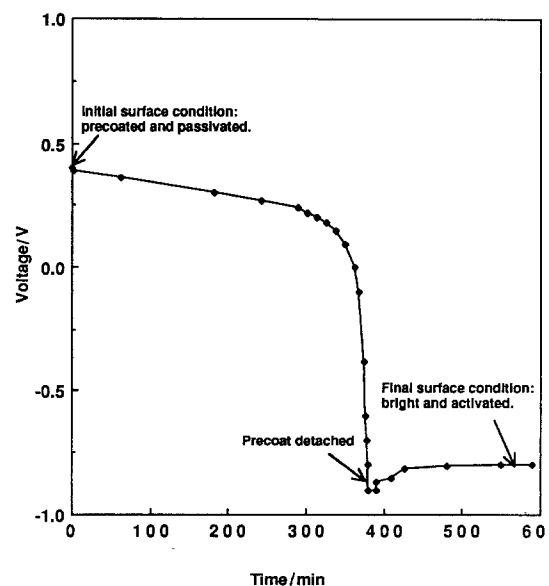


Fig. 4. Voltage of the passivated sample 3a during cathodic reduction at  $-5 \text{ mA cm}^{-2}$ . The EMD deposit was scraped before cathodic reduction.

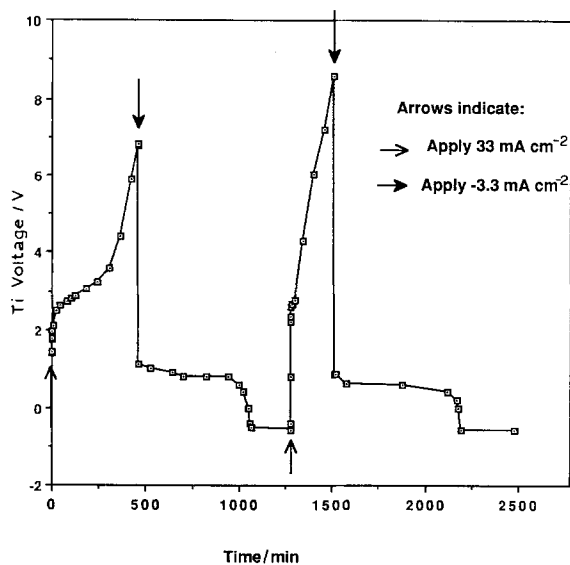


Fig. 5. Voltage of titanium anode during EMD deposition and subsequent cathodic reduction. The anode had initially a  $50\ \mu\text{m}$  thick precoating layer.

deposition cycle shows a faster rise in voltage than the first deposition cycle. This is because no precoating was present on the titanium surface prior to the second deposition cycle.

Sample 2d, passivated as shown in Fig. 2d, was cathodically reduced after scraping the EMD deposit. The voltage behaviour during reduction is shown in Fig. 6a. It is seen that at least 130 min are needed to reach the activated state. This time is more than five times greater than that expected if one were to reduce separately the oxidized surface and the unoxidized

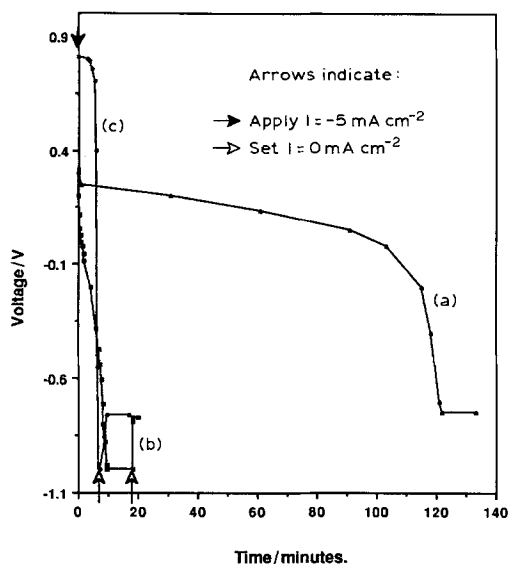


Fig. 6. Voltage of titanium anodes with different surface conditions during cathodic reduction at  $-5\ \text{mA cm}^{-2}$ . (a) Passivated pre-coated Ti (30 min); (b) passivated nonprecoated Ti, (c) as-precoated Ti (30 min).

surface with the same thickness of precoat (Fig. 6b and c, respectively). Figure 6b corresponds to a non-precoated sample passivated to 16 V and reduced after scraping the EMD deposit, and Fig. 6c corresponds to a sample reduced in the as-precoated condition (30 min of precoating). The observed large difference in reduction time between samples 6a and 6b may be related to the rate at which the oxide grows on each sample during EMD deposition. Oxides grown at different rates have shown to have different degrees of stability [11, 12]. Because of the precoating layer, one expects the rate of oxide growth on sample 6a to be much smaller than that on the unprecoated sample 6b.

#### 4. Conclusions

Titanium pre-coated with a thin layer of  $\text{MnO}_2$  was found to experience a delay in passivation depending on the initial state of the surface. Samples pre-coated in the activated condition showed a considerable delay in voltage rise relative to those pre-coated in the non-activated condition. Cathodic reduction applied to passivated pre-coated titanium caused detachment of the precoat and reduction of the passivating film. Based on the reduction time necessary to activate titanium, the reduction rate of a passivating film grown on pre-coated titanium is inferred to be much smaller than that of a film grown on unprecoated titanium.

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