

## CATHODIC BEHAVIOUR OF ANODIZED TITANIUM IN SIMULATED PHYSIOLOGICAL CONDITIONS

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**Abstract** — In the present work, anodic oxide films on titanium specimens were formed in physiological solution under potentiostatic condition. The immediate- to short-term changes in the oxide film were studied by open-circuit potential measurements and cyclic voltammetry. The results show that the intensity of the cathodic current peak related to oxygen reduction at around  $-0.7$  Vsce, decreased and disappeared after 30 minutes of finishing the anodic oxidation. For titanium without anodization (non-coated titanium), the cyclic voltammograms show an anodic current in the range that begins at  $-0.9$  Vsce and continues to more positive potentials (vs SCE), related to the hydrogen oxidation reaction. For anodically polarized titanium (coated titanium), in the anodic direction of the cyclic voltammograms an anodic current in the range that begins at  $-0.9$  Vsce and continues to more positive potentials (vs SCE) was observed. In this case, the oxidation process is related to previous cathodic processes: the hydrogen formation and the cathodic transformation of titanium oxides before the oxygen reduction potential region.

**Keywords**— Cathodic Behaviour, Cyclic Voltammetry, Anodized Titanium, Titanium Oxide.

### I. INTRODUCTION

Titanium, one of the most important materials used for many years as biomedical and dental implant applications, has an excellent corrosion resistance in many aqueous environments because of its oxide film, which has been shown to be highly stable and fairly non-reactive. Due to its excellent corrosion resistance, titanium is often included as a benchmark in the corrosion studies of biomedical alloys. Many investigations have shown that this type of natural surface film is normally a few nm thick and essentially formed by a thin layer of amorphous  $\text{TiO}_2$ , however, different oxides ( $\text{TiO}$ ,  $\text{TiO}_2$ ,  $\text{Ti}_2\text{O}_3$ ,  $\text{Ti}_3\text{O}_5$ ,  $\text{TiO}_3$ ) may also be present (Frauchiger *et al.*, 1997; Lausmaa *et al.*, 1990; Pan *et al.*, 1996).

Among other factors, the oxidation state of titanium in the oxide and, consequently, its stoichiometry and its surface characteristics are dependent on the final positive potential and on the electrolyte used for the oxide growth (Frauchiger *et al.*, 1997; Kuromoto *et al.*, 2007; Marino *et al.*, 2001; Pan *et al.*, 1996). Blackwood *et al.* (1988) found that the oxide film undergoes uniform

dissolution and its stability depends strongly on the rate at which it has been formed. These authors also reported that the growth rate has a marked influence on the properties of anodic oxide film on titanium (Blackwood and Peter, 1989).

There are a few possible explanations for the origin of cathodic peaks between 0.0 and  $-1.0$  Vsce. For example, the formation of lower valence states such as  $\text{Ti}^{3+}$  in the anodic oxide film of  $\text{TiO}_2$  may be associated with such a cathodic reaction (Baez *et al.*, 1992; Kim *et al.*, 2003). Baez *et al.* (1992) explained the cathodic current peak in terms of the formation of  $\text{Ti}^{3+}$  at the uppermost monolayer (or multi-layers) of the oxide film. The formation of titanium hydroxide may also be related to such a redox reaction, which forms the outermost layer of the oxide film (Kim *et al.*, 2003). Another possible explanation is the reduction of  $\text{H}^+$  ion, which is adsorbed on and absorbed in the film at the underpotential deposition region (Yoon and Pyun, 1995). Azumi and Seo (2001) found a transformation of  $\text{TiO}_2$  to unstable titanium peroxides such as  $\text{TiO}_3$  above 3 Vsce. These compounds are reduced below 0.5 Vsce and showed a characteristic cathode current peak. In a previous work, the authors (Pelaez-Abellan *et al.*, 2007) found a cathodic peak around  $-0.4$  Vsce in aerated simulated physiological solution due to the reduction of titanium peroxides such as  $\text{TiO}_3$ .

The reduction of oxygen may occur at negative potential also. Parkinson *et al.* (1980) reported only one wave at a rather negative potential. In contrast, two other authors (Clechet *et al.*, 1979; Danzfluss and Stimming, 1984) have reported a well defined reduction wave at less negative potential and evidence was presented that hydrogen peroxide was formed. There are clearly several disparities between conclusions drawn from these studies, due to differences in experimental conditions. Baez *et al.* (1992) proved that the reduction of oxygen could occur at a more negative potential than the reduction reaction of titanium oxide and they suggested that this surface redox process take place at most in a few monolayers of titanium oxides. In all materials, the potential for oxygen reduction appears to coincide with the potential range where the cyclic voltammetry in the absence of  $\text{O}_2$  would indicate the reduction of the titanium oxide.