Preparation, Study and Modification of Nanometer-Scale Flat TiO_2 Surfaces by Electrochemistry and AFM Techniques

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In order to study local properties of surfaces, it is necessary to control their preparation mode to get reproducible and well characterized samples. The first part of this work concerns the preparation of TiO_2 films on Ti substrates that fulfil these criteria.

The TiO_2 formed by anodisation of titanium is a n-type semiconductor, *i.e.* anodic reactions are blocked. However, the reactivity of the electrodes towards redox species in solution can be enhanced considerably by electrochemical deposition of a second metal with catalytic properties such as platinum (1,2). The second part of this work is devoted to the preparation and the study of TiO_2/Ti electrodes "modified" by a Pt-deposit.

PREPARATION OF TiO_2/Ti ELECTRODES

Titanium disks (Goodfellow; purity: 99.99%) were fixed on a Teflon holder mounted on a rotating electrode operating at 2000 rpm, and introduced in a Dewar containing methanol, n butanol and $HClO_4$ at -35°C (3). The disks were electropolished by applying a potential of 22 V between the Ti anode and the Pt counter-electrode for a duration of 200 s. Such a procedure gave highly reproducible flat Ti surfaces, as it was confirmed by AFM measurements. The samples were studied with a Digital Instruments Nanoscope III atomic force microscope, both in Contact mode and Tapping® mode. The roughness parameter R_{rms} was about 12 nm.

Thus, the anodic oxidation of the samples was performed in 0.5 M H_2SO_4 with a galvanostat ($j = 8.2$ mA cm^{-2}) until a potential difference of 10 V was reached between the Ti sample and the Pt counter-electrode. The aim of anodisation is to provide a reproducible passivating layer. It's thickness is estimated to be 35 nm (1).

PLATINUM DEPOSITION

Platinum was electrodeposited on the flat Ti surfaces at ambient temperature from a $Pt(NH_3)_2(NO_2)_2$ solution (10 g L^{-1}) in 0.5 M H_2SO_4 during 100, 300, 500 or 1000 s at -0.1 V *vs* Ag/AgCl.

Typical AFM images of Pt deposits obtained after 100 s and 500 s of deposition time are presented in Figure 1.

For "100 s" and "300 s" Samples, the Pt deposits appear as hemispherical isolated particles with heights between 40 and 80 nm. These particles are homogeneously distributed on the substrate (see Fig. 1A). For Samples "500 s" and "1000 s", the surface is fully covered with Pt agglomerated clusters with heights between 200 and 500 nm (See Fig. 1B).

ELECTROCHEMICAL BEHAVIOR OF Pt/TiO_2/Ti ELECTRODES

All the experiments were performed in 1 M KCl solution containing hexacyanoferrates: $[Fe^{II}] = [Fe^{III}] = 10^{-2}$ M. Quasi-stationary I-E curves were plotted in the potential range -200 to +300 mV *vs* Ag/AgCl. The rate constants and the exchange current densities were determined from that curves. For the TiO_2/Ti electrode without Pt, j_0 is very small ($j_0 = 7\ 10^{-13}$ A cm^{-2}); as TiO_2 is a n-type semi-conductor, anodic reactions are blocked. However, on Pt/TiO_2/Ti electrodes, both cathodic and anodic reactions are observed; the exchange current density, referred to the total geometric area, is about 10^5 times greater than that of the TiO_2/Ti electrode. It is deduced that the anodic reactivity has been considerably enhanced by the Pt deposit. However, j_0 is about 100 times lower than that obtained with pure platinum ($j_0 = 2\ 10^{-3}$ A cm^{-2}).

The anodic limiting diffusion current I_{lim} was compared for a Pt electrode and Pt/TiO_2/Ti electrodes. As I_{lim} is proportional to the electroactive area, one can deduce that the whole surface is not active in the modified electrodes. For example, with Sample "500 s", only 70% of the electrode is active although the surface seemed to be completely covered with Pt.

In addition, the curves I/I_{lim} *vs* overvoltage were plotted for Pt and Pt/TiO_2/Ti electrodes. The steeper slope of the Pt-curve (when $\eta \rightarrow 0$) shows that the redox reaction proceeds faster.

Previous results obtained by impedance spectroscopy (3) were confirmed. Reaction proceeds slower on Pt/TiO_2/Ti electrodes; several elements in series must be considered in the equivalent circuit for interpreting the diagrams:

(i) a resistance R_s (mainly the electrolyte resistance)

(ii) a loop (C_{ox}, R_{ox}) corresponding to the contribution of the underlying TiO_2 layer

(iii) a loop (C_{dl}, Z_F) corresponding to the double layer capacitance in parallel with the faradaic impedance.

For Pt electrodes, only (i) and (iii) have to be considered.

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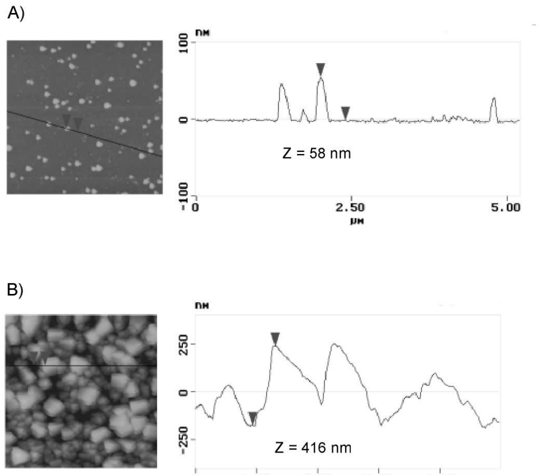

Figure 1: AFM images and cross sections of Pt-deposits on titanium surfaces
A) Sample "300 s"
B) Sample "500 s"

Dimensions: 5 µm × 5 µm