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# Electrocatalytically Relevant Surface Properties of Anodic Oxides: $TiO_2$

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Photoelectrochemical, electrochemical, surface structural and compositional studies of Ti||$TiO_2$ and $RuO_2$||$TiO_2$ interface are described. Anodic $TiO_2$ films formed on Ti substrate revealed the presence of *rutile* as the only identifiable phase. A kind of epitaxial relationship between the titanium substrate and slowly grown $TiO_2$ films was established. Thermally applied $RuO_2$ on the anodic films acted as a probe for the microstructure of $TiO_2$. $RuO_2$ exhibited electrocatalytic and photoelectrochemical effect on slowly grown oxide films and showed none on step grown films. XPS and LEED studies of single crystal $RuO_2$ and $RuO_2$||Ti interface showed that vapor deposited titanium reduces the always present $RuO_3$ on the surface layers of $RuO_2$. The pseudomorphism of rutile $RuO_2$ and $TiO_2$ yielded eventually to an epitaxial ordering of $TiO_2$ overlayer. The structures of the order $TiO_2$ overlayers at the (100) *versus* the (110) face of $RuO_2$ were interpreted by the difference in their atomic arrangement.

## 1. INTRODUCTION

Among the many oxides which play important roles in electrocatalysis nowadays, we will focus our attention to $TiO_2$. The oxide is widely studied and its properties are widely exploited in the field of electrochemistry. Anodically $TiO_2$ is formed on and with the participation of the titanium substrate as a component. As a substrate titanium is known as inert. However, the chemical stability of titanium is due to the presence of $TiO_2$ as an inert oxide on its surface.

The most important properties of $TiO_2$ in connection with electrocatalysis are those related to its combination with $RuO_2$. In this combination, better known under the trade name of DSA, $TiO_2$ serves as a component and as a support for the catalytically active $RuO_2$. In order to get an insight in the interaction of $RuO_2$ and $TiO_2$, the surface properties of $TiO_2$ which

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are of interest in this study will mostly have the correspondent properties of $RuO_2$ given in parallel. However, the relevance of the facts and their interpretation is not limited by the scope of this paper. $TiO_2$ constitutes the solid phase at the interface of titanium in contact with an aqueous electrolyte. The knowledge of the surface properties of $TiO_2$ revealed here could be of interest for understanding the liquid part of the double layer structure, while the structural and compositional data could help the understanding of the potential distribution in the solid portion of this semiconducting material.

The content of the paper will mainly be based on the novelties in the methodology, results and interpretation of our research in this field. By the origin of the formation, the types of $TiO_2$ considered here will be classified in three categories:

— thin, anodic films on titanium substrate;
— evaporated submonolayer and monolayer titanium on single crystal $RuO_2$ substrate;
— films obtained *via* thermal decomposition of suitable titanium salts.

The investigation of the first of these categories of $TiO_2$ films were intended to reveal the substrate (Ti)-oxide ($TiO_2$) relationship. The properties of the $TiO_2$ film adjacent to the substrate are often indicated as the most important for the failure of the $RuO_2$-$TiO_2$ electrocatalysts. While the $TiO_2$ film protects the substrate from corrosion, the high electric resistivity of the film might be a cause of a break potential build up during the anodic current passage.

The $TiO_2$ films formed on single crystal $RuO_2$ substrates were studied in order to obtain direct information on the interaction of $RuO_2$ and $TiO_2$ at their interface.

The class of $TiO_2$ films with or without $RuO_2$ formed by thermal treatment of easily decomposable salts served not only to test the applicability of the data obtained on a more fundamental level but also to probe the properties of the anodic $TiO_2$ films.

The experimental methods applied for the investigation of the properties of the $TiO_2$ films can again be classified in three groups. Photoelectrochemical methods were mainly used in the studies of the anodically grown films. The experimental work at the $RuO_2||TiO_2$ interface was performed in ultra high vacuum conditions (UHV) with the use of X-ray photoemission spectroscopy (XPS), low energy electron diffraction (LEED), and Auger electron spectroscopy (AES). Electrochemical techniques such as cyclic voltammetry were used for testing the oxide films obtained *via* thermal routes.

Even though two interfaces are crucial for the determination of catalytically relevant properties of $TiO_2$, $Ti||TiO_2$ and $RuO_2||TiO_2$ interface, three types of $TiO_2$ films and three groups of experimental methods were distinguished above. Consequently, the presentation of the data along with pertinent experimental details would be divided in three parts. In the first part the properties of the $Ti||TiO_2$ interface will be in focus, while those of the single crystal $RuO_2||ViO_2$ interface will be treated in the second. The third part will deal with polycrystalline, thermal $RuO_2||TiO_2$ anodic films. The latter might be considered as the closest to the practical electrocatalysts, where many $RuO_2||TiO_2$ interfaces of random orientation and physical dimensions are encountered.

## 2. $Ti||TiO_2$ INTERFACE

Information on the $Ti||TiO_2$ interface were gathered by studying the relationship between the titanium substrate and the anodic $TiO_2$ film formed on this substrate. Both structural and photoelectrochemical studies were carried out on these films.

*Anodic oxide film formation.*[1-3] Thin, slowly grown anodic films were obtained by ramping the titanium electrode potential from the open circuit potential to the designated value (0.1 mV/s potential ramp, up to 10 V). This oxide growth rate is the lowest reported in the literature. Near to equilibrium conditions between the titanium substrate and the forming film were intended. Additionally, the oxide growth rate under these conditions (current densities $\lesssim 2\ \mu A/cm^2$) is probably the closest to the real situation for anodic $TiO_2$ film formation where only negligible fraction of the catalytic current goes towards titanium oxidation.

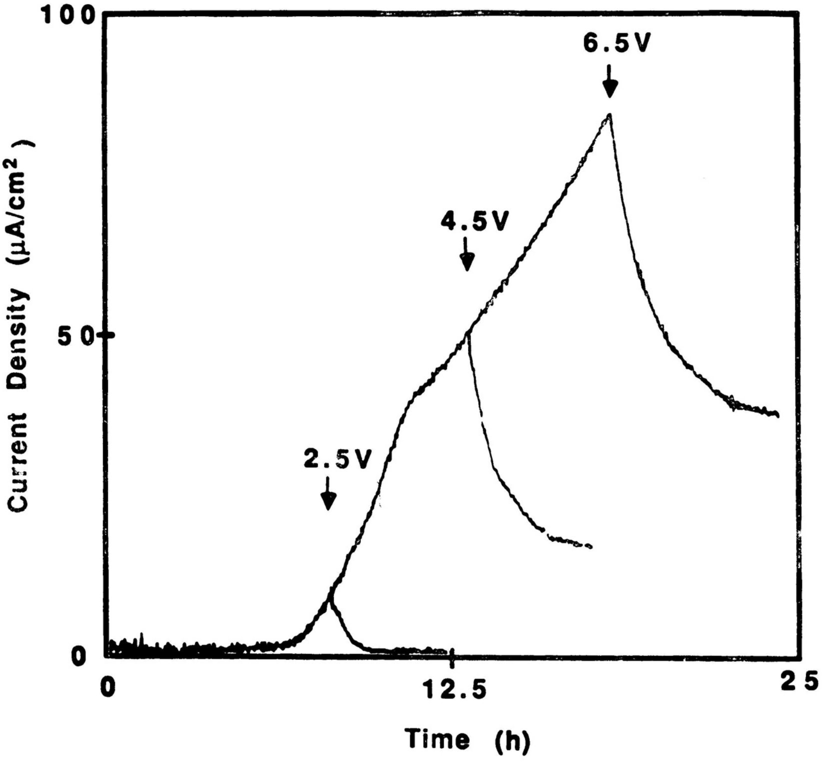

Figure 1. $TiO_2$ growth curves. Anodic current *vs.* time/potential on polycrystalline titanium substrates at 0.1 mV/s to the final potentials (indicated) at which the samples were kept for additional four hours. The potential ramping started at an open circuit potential of approximately —0.3 V (SCE); 0.05 M $H_2SO_4$.

Following the mechanical polishing and immediately prior to anodization, all samples were etched for 3—4 seconds in solution of 1% HF and 3% $HNO_3$. Carefully prepared samples exhibited reproducible growth curves (Figure 1).

Samples grown at higher rate (potential scan rate of 1 mV/s) as well as step grown samples served for comparison.

*Structural findings.*[2] Transmission electron microscopy (TEM) and reflection electron diffraction (RED) studies have shown that *rutile* is the only identifiable phase in all the films studied. For slowly grown films on polycrystalline titanium an ordered oxide structure is present with a preferential growth direction [110] on some substrate grains. As the oxide growth rate is increased the film structure becomes more homogeneous and the average crystallite size decreases.

*Photospectroscopy studies.*[3-5] Two types of photoelectrochemical studies were performed in order to reveal the structural and electronic properties of the $TiO_2$ films: spectroscopy of the large surface area (0.2 $cm^2$) and localized ($2 \times 10^{-7}$ $cm^2$). Bandgap analysis of the photospectroscopy data shows a small shift of the indirect bandgap and a disappearance of the direct bandgap at higher oxide growth rate (Figure 2). The loss of the direct bandgap at more rapidly grown oxide we have attributed to a decrease in the long range ordering of the rutile film, which is in contrast to suggestions in the literature of a transition of the rutile to an amorphous structure. This is in agreement with the RED and TEM results interpreted as crystallinity decrease with the growth rate.

*Photoelectrochemical microscopy (PEM).*[1-6] PEM has recently been introduced as an *in situ* technique for studying fundamental properties of thin

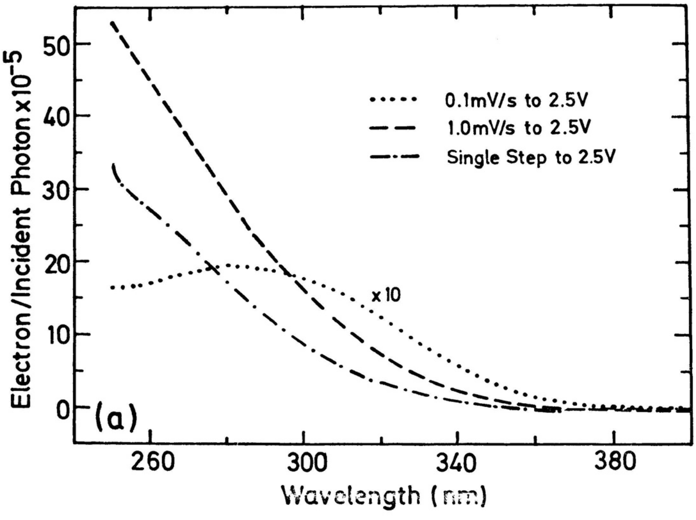

Figure 2.

*Fig. 2. to be continued*

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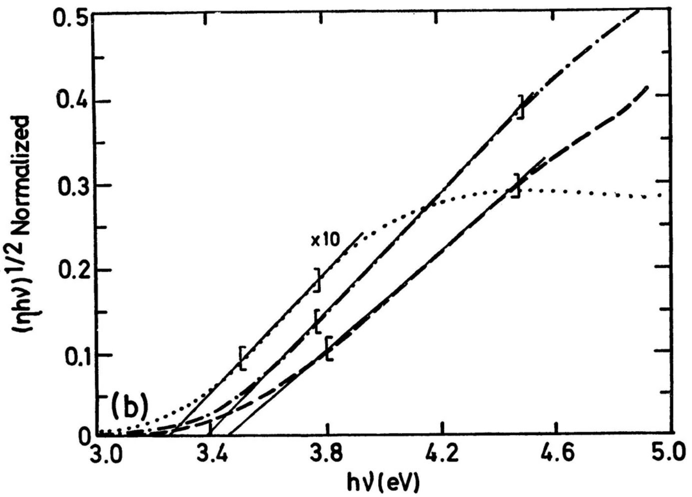


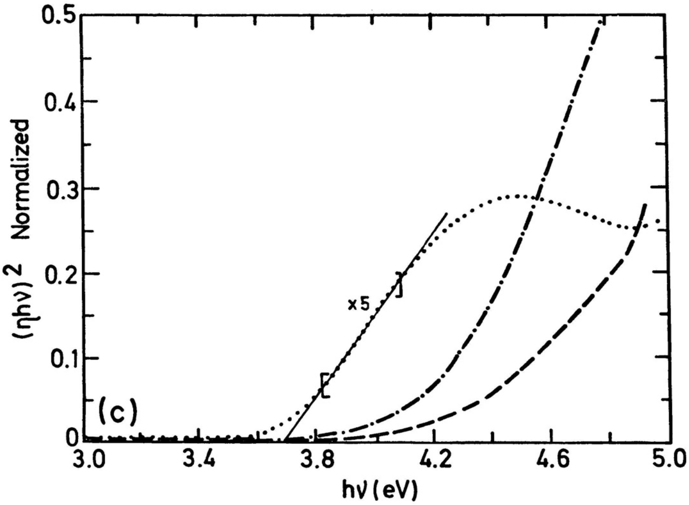


Figure 2. (a) Photospectroscopy data for anodic $TiO_2$ films grown to 2.5 V at different potential ramping rates; Electrode potential bias: 1 V (SCE); (b) Direct bandgap plots; (c) Indirect bandgap plots. According to Butler's photoeffect theory (see ref. 2 for details), the photoresponse of a crystalline semiconductor is given by $\eta h\nu = \text{const}\ (h\nu - E_g)^{n/2}$; $\eta$-quantum efficiency; $E_g$-bandgap; n = 1 for a direct and n = 4 for an indirect transition.

anodic oxide films on polycrystalline substrates. Photocurrents are measured locally using a rastered laser beam which is focused to a small spot (~ 20 $\mu m^2$). Variations in the photocurrent reveal changes of the oxide properties with a spatial resolution determined by the size of the light spot (Figure 3).

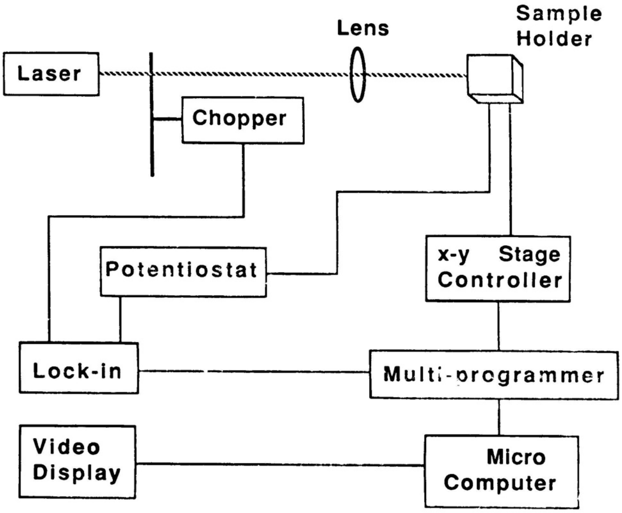


Figure 3. Photoelectrochemical Microscopy (PEM): aparatus and description. Cell: 2 mm thick fused silica window; 5 mm electrolyte (0.05 M $H_2SO_4$); the cell was mounted on a computer controlled X—Y table with 0.1 μm resolution. The actual resolution was determined by the microscope objective (5 μm). Argon ion laser: 351/364 nm, 0.1 mW. PEM images were formed by rastering the light spot across 2 × 1.6 mm area of the sample at 60 μm/s (50,000 data points, 8 μm increments in both directions).

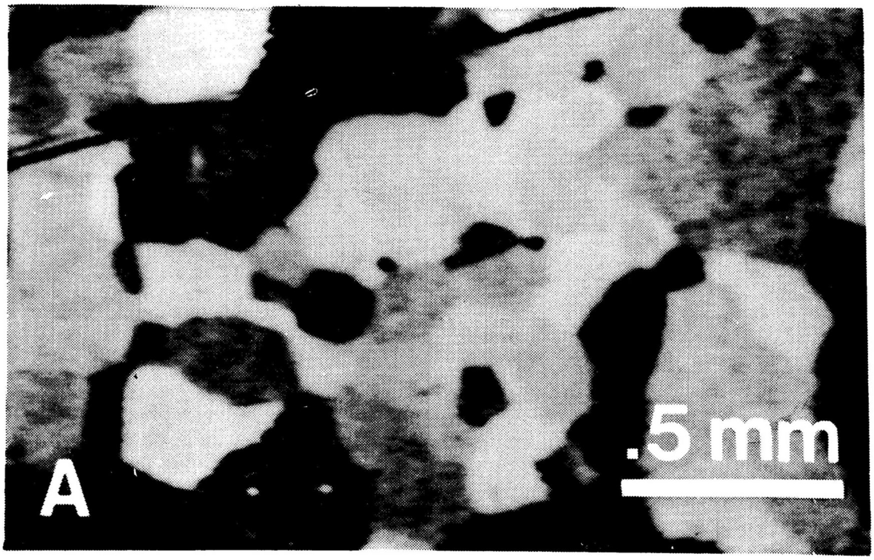


Figure 4. Photoelectrochemical image of anodic $TiO_2$ film grown to 3.5 V at 0.1 mV/s. The image was created by grouping the 50,000 data points in 151 shades on the gray scale. The areas with the same photocurrent intensities correspond to the crystal grains of the polycrystalline titanium substrate.

The localized photoresponse of the oxide film on polycrystalline titanium (producing an image of different photoresponses) was found to be heterogeneous for slowly grown films (Figure 4). These heterogeneities are clearly associated with the grain structure of the underlying metal substrate. The photocurrent contrast ratio observed for images of slowly grown film is independent of the average film thickness. As the oxide growth rate is increased, both the average photocurrent and the photoresponse heterogeneity decreases (Figure 5).

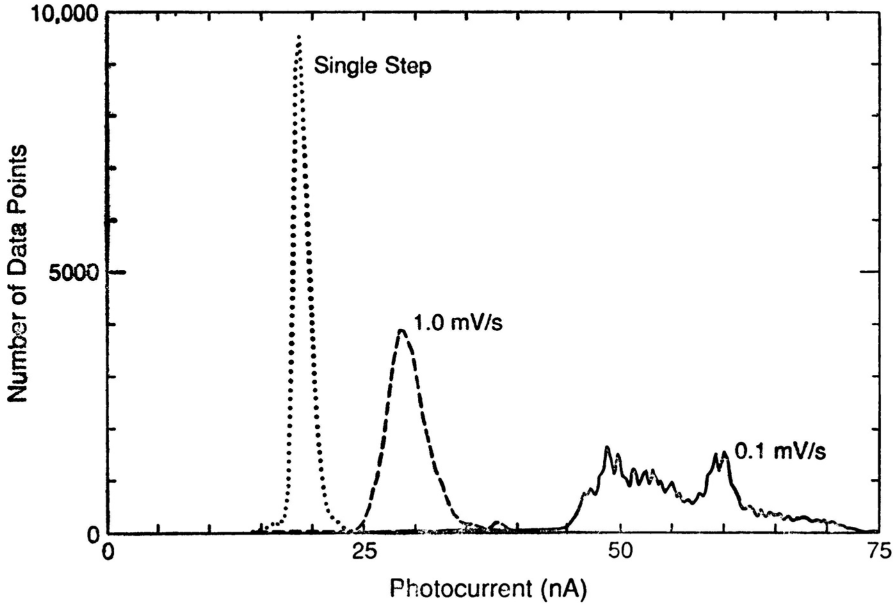


Figure 5. Histograms of photoelectrochemical images (50,000 data points each) for anodic $TiO_2$ films grown at different potential rate; final growth potential: 2.5 V; electrode potential bias: 1 V SCE. Note that both the photoresponse and the contrast ratio decrease as the growth rate increases.

*Local thickness determination by AES.*[5] Auger depth profiling showed a linear dependence of the oxide film thickness on the final growth potential (Figure 6). However, in order to elucidate further the nature of the local photoresponse heterogeneity, Auger depth profiling on spots with already identified photoresponses were performed. The variations in the oxide film thickness from one crystal grain to another were within $\pm 8\%$ while the photocurrents at the same spots varied as much as 1 : 1.7 (Table I). While the film thickness was uniform throughout the sample, only the photoresponses within the same crystal grain were uniform.

*Summary of the structural and photoelectrochemical findings on anodic $TiO_2$ films.* The following explanation is proposed for the connection between the crystal structure, the substrate grain structure, and the oxide photoresponse. For slowly grown $TiO_2$ films, an ordered growth of the oxide on the titanium substrate may occur for some substrate grains. This would result

TABLE I

*Variations in the $TiO_2$ film thickness and the photocurrents at the same spots at different crystal grains*

| Crystal grain | film thickness (nm) | photo-current (μA) |
|---|---|---|
| 1 | 15.5 | 123 |
| 2a | 17.0 | 140 |
| 2b | 17.0 | 143 |
| 2c | 16.5 | 133 |
| 3a | 15.0 | 88 |
| 3b | 15.0 | 88 |
| 4 | 15.5 | 138 |
| 5 | 17.5 | 130 |
| avg. | 16.2 | 123 |
| Δ/avg. | 0.15 | 0.44 |

in an oxide film with large grains and a low grain boundaries volume. For other substrate grains, the nucleation of oxide crystallites occurs in a more random fashion and the result is the formation of a more disordered film with smaller crystallites and a larger grain boundaries volume. It is further proposed that the grain boundaries in the oxide serve as recombination sites for electron — hole pairs and the quantum efficiency of the oxide is lowered as the number of recombination sites increases. Ordered oxide films should consequently exhibit a higher photoresponse than films with a more crystallite structure. We therefore propose that the observed

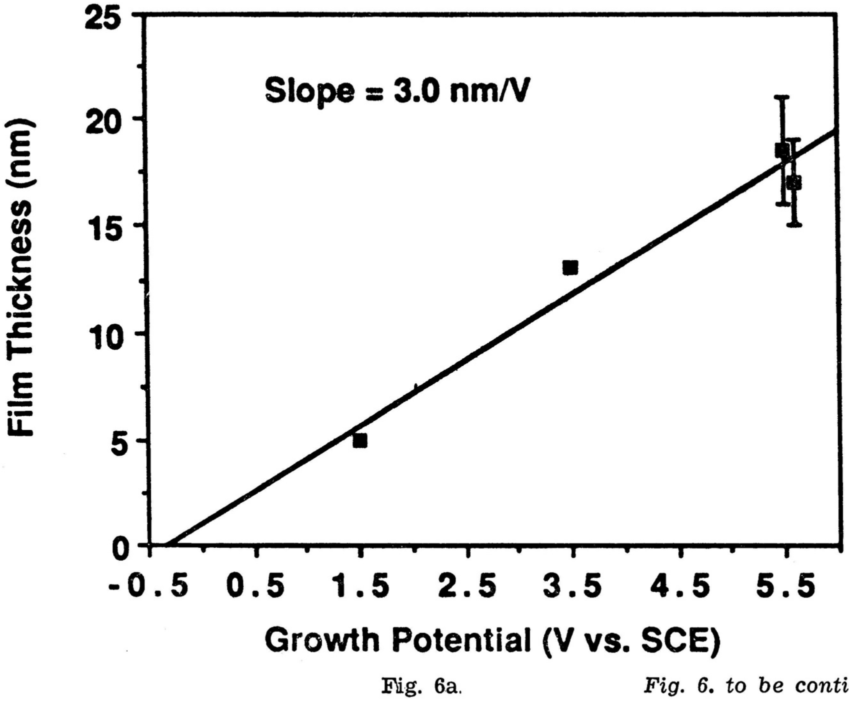


Fig. 6a.

*Fig. 6. to be continued*

Fig. 6. *continued*

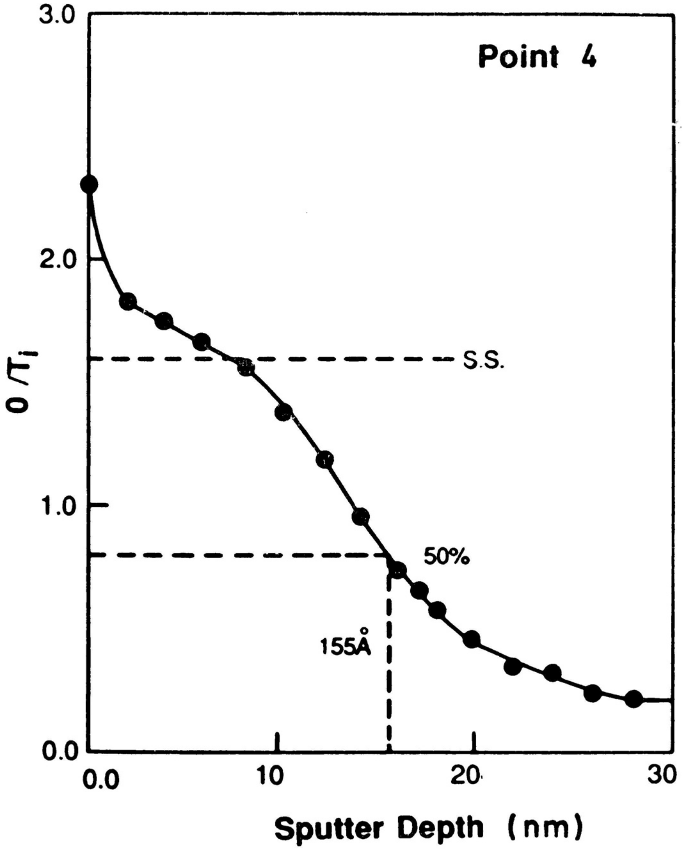


Figure 6. (a) Film thickness dependence on growth potential determined by Auger depth profiling ramping rate: 0.1 mV/s; (b) Typical Auger depth profile of anodic $TiO_2$ films grown to 2.5 V (point 4 in Table I).

heterogeneities in the PEM images are due to different oxide ordering on different titanium substrate grains. A type of epitaxial growth of the oxide occurred in which the oxide crystal orientation is dependent on the substrate structure.

One might argue that due to thinness of the $TiO_2$ films the heterogeneties in the photoresponses could simply be a result of the variations in the reflectivity of different substrate grains. This explanation is not acceptable since (*i*) the extent of etching influences the optical reflectivity of the substrate, but does not alter the photoresponses, and (*ii*) the substrate reflectivity is not expected to change with oxide growth rate.

### 3. $RuO_2||TiO_2$ INTERFACE

*Single crystal $RuO_2$ surface.*[8] The understanding of the surface properties of $TiO_2$ is added by studying the structure and the chemical composition of single crystal surfaces of $RuO_2$. $RuO_2$ crystallizes only as a rutile with lattice parameters very close to the $TiO_2$ rutile structure. [110] plane of pure $RuO_2$ is the one which is most frequented. Surface ordering related to the oxygen content at the top layers was found (Figure 7). It is important to point out that, regardless of the oxygen content, a presence of a defect $RuO_3$ structure in all identified $RuO_2$ surface structures was found.

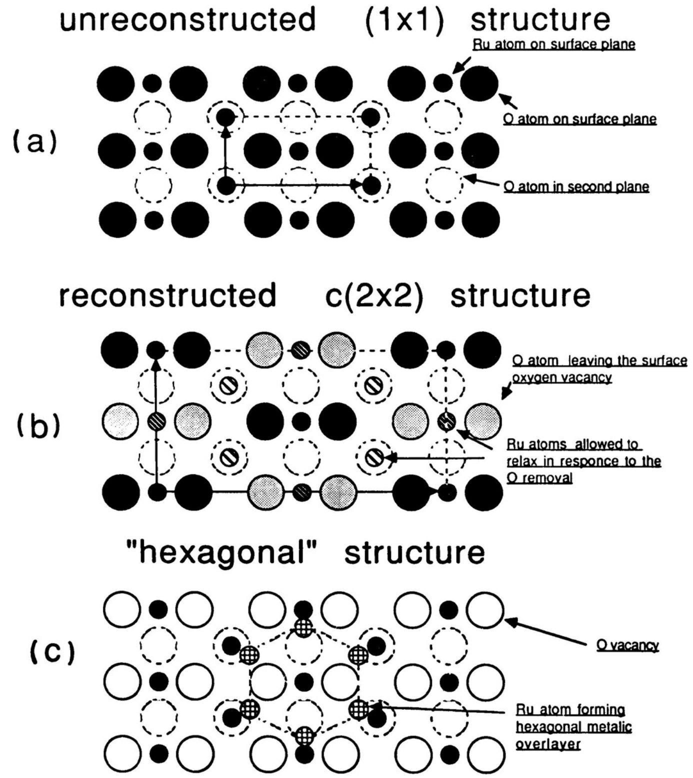


Figure 7. Surface ordering of (110) $RuO_2$ single crystal as a function of the surface oxygen content; (a) unreconstructed (1 × 1) which corresponds to stoichiometric $RuO_2$; (b) centered (2 × 2) with medium surface oxygen content; (c) hexagonal reconstruction representing ruthenium overlayer with practically no surface oxygen. The surface structures are reversible with the surface quantity of oxygen according to the following scheme:

$$(1 \times 1) \quad \underset{450\ ^\circ\text{C, O}_2}{\overset{450\ ^\circ\text{C, UHV}}{\rightleftarrows}} \quad c\ (2 \times 2) \quad \underset{450\ ^\circ\text{C, O}_2}{\overset{450\ ^\circ\text{C, UHV}}{\rightleftarrows}} \quad \text{hexagon}$$

*Titanium substrate — $RuO_2$ interaction.*[9] The epitaxial relationship between the titanium substrate and $TiO_2$ and the finding that *rutile* is the only identifiable phase of $TiO_2$ can be put in correlation with the direct studies of the titanium substrate — $RuO_2$ interface. The studies were performed in an UHV system. The roles of titanium as a substrate and $RuO_2$ as a catalyst for this purpose were changed. Namely, monolayer quantities of titanium were vapor deposited on single crystal surfaces of $RuO_2$. It was found that following the oxidation of titanium $TiO_2$ orders epitaxially. The ordering procedure is dependent on the $RuO_2$ planes orientation. It takes several monolayers of $TiO_2$ and temperature up to 600 °C in order to achieve a well defined LEED pattern on $RuO_2$ [110] plane, while the ordering on $RuO_2$ [100] is achieved with less titanium and at lower temperatures. The interpretation of these findings requires that the question of reactivity of both titanium and ruthenium with oxygen available at the plane level to be addressed. Due to its importance for the stability of the electrocatalyst, we devote more space to considerations of the chemistry and structure of the $RuO_2||Ti$ interface.

As we have stated previously,[8] $RuO_3$ seems to be in equilibrium with $RuO_2$ ond $O_2$ on the surface of $RuO_2$. $RuO_3$ plays an important role in the decomposition of $RuO_2$ and for that matter in the stability of the whole catalyst. We believe the following gross reaction scheme involving $RuO_3$ occurs at the Ti interface with the reduced, disordered $RuO_2$ surface:

$$5Ti + 3RuO_3 \longrightarrow Ti_2O_3 + 3TiO_2 + 3Ru \qquad (1)$$

The oxygen interstitials from the $RuO_3$ defect sites are expected to diffuse and react with Ti more readily than the oxygen anions from the $RuO_2$ lattice.

On the oxygen saturated, ordered $RuO_2||Ti$ interface, a plausible reaction scheme is:

$$Ti + 2RuO_3 \longrightarrow 2RuO_2 + TiO_2 \qquad (2)$$

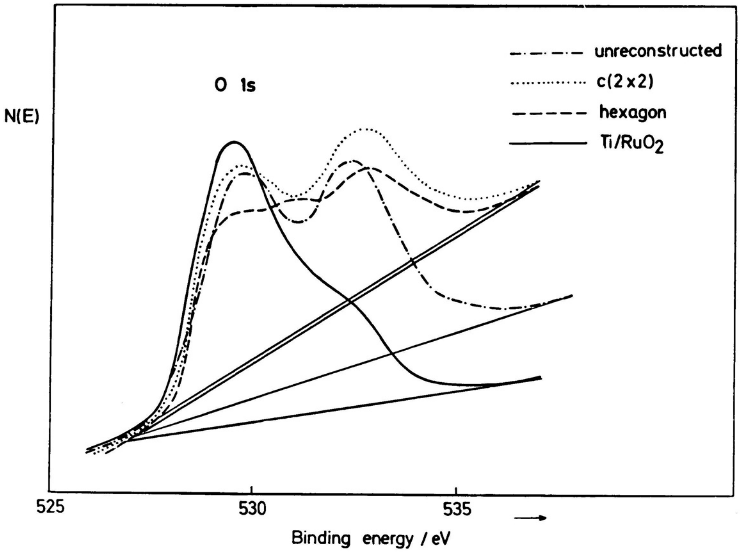
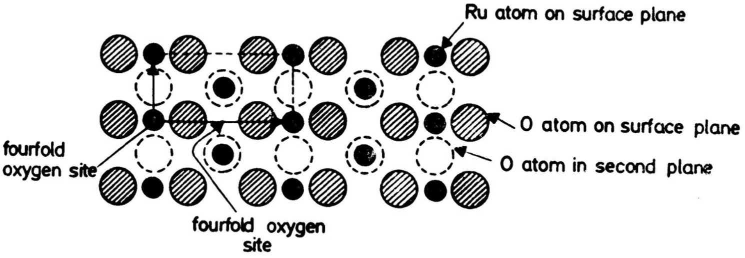
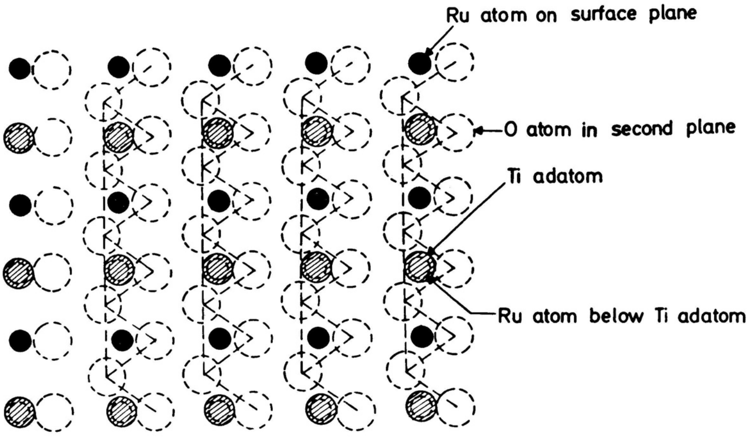


Figure 8. Oxygen 1s XPS region of unreconstructed (1 × 1), centered (2 × 2) and hexagonal reconstruction of (110) $RuO_2$ single crystal and $RuO_2$ with Ti overlayer. The O 1s peak attributed to the $RuO_3$ (the saddle in the middle) is reduced at the interface with Ti.

The reaction of Ti at the stoichiometric $RuO_2$ surface proceeds with the $RuO_3$ species as evidenced by the O 1s photoemission (Fig. 8). The O 1s peak attributed to the $RuO_3$ sites are the primary targets of Ti chemical attack. This assumption is supported by LEED evidence. Due to the absence of the $RuO_3$ defect structure, the quality of the LEED pattern exhibited at the interface improves comparing to the pure $RuO_2$.



UNRECONSTRUCTED (1x1) STRUCTURE
$RuO_2$ (110) face



RECONSTRUCTED (1x2) STRUCTURE
$RuO_2$ (100)/Ti interface

Figure 9. Real space schematic interpretations of the geometric structures developed at the $RuO_2||Ti$ interfaces; (a) two diffracting domains of the (1 × 1) epitaxial $TiO_2$ overlayer on the $RuO_2$ (110) orientation; (b) the (1 × 2) $TiO_2$ overlayer periodicity on the $RuO_2$ (100) face.

The easiness of the titanium overlayer ordering at the (100) plane *versus* the (110) face can be explained by the difference in their atomic arrangement. The topmost $RuO_2$ (110) surface monolayer plane comprises both oxygen and ruthenium atoms. The $RuO_2$ (100) orientation is assembled by the alternate planes build up of only Ru atoms or only O atoms. The $RuO_2$ (100)

face preferentially terminates with the plane constituted of ruthenium atoms. The absence of oxygen in the topmost surface monolayer of the (100) face should decrease the amount of the defect structure $RuO_3$. Hence, the contribution of the ordered rutile structure is improved. The top-most layer composed of Ru atoms having a good quality of two dimensional periodicity is a convenient substrate for the growth of an ordered overlayer.

The formation of the rutile $TiO_2$ was not necessary in order to get the periodic arrangements of the adatoms on the rutile substrate. We may speculate that the $(1 \times 2)$ unit mesh of the overlayer is created favorably due to the preferential resting of titanium adatoms at threefold sites of oxygen atoms in the second plane (Figure 9). The Ti adatoms, competing with the native Ru atoms, occupy these sites in such way as to attain the maximum coordination with the oxygen atoms. This can be accomplished only if the triangular oxygen clusters surrounding Ti adatoms do not overlap. The condition to have one triangular oxygen cluster for each Ti adatom is satisfied at every cation site of the rutile lattice along the $< 110 >$ direction and at every second cation site along $z$ direction. The resulting periodic arrangement of the Ti overlayer produce $(1 \times 2)$ LEED pattern.

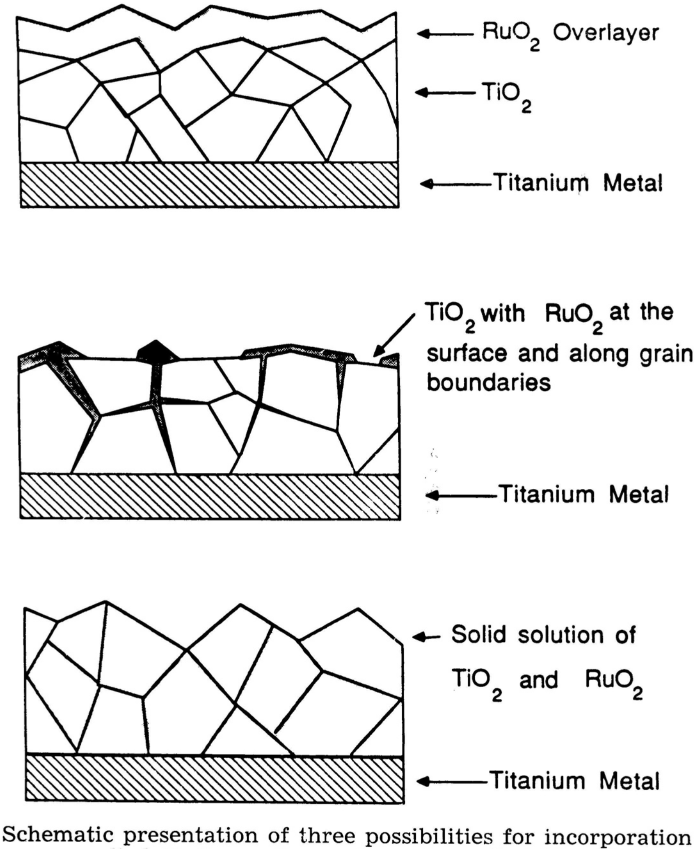


Figure 10. Schematic presentation of three possibilities for incorporation of thermally applied $RuO_2$ on the surface of anodic $TiO_2$ films.

As for the stability, the newly formed Ti-O bonds are stronger and less susceptible to the thermally induced cleavage than the Ru-O bonds. The Ti-O bonds prevent the release of oxygen into vacuum and increase the stability of the interface.

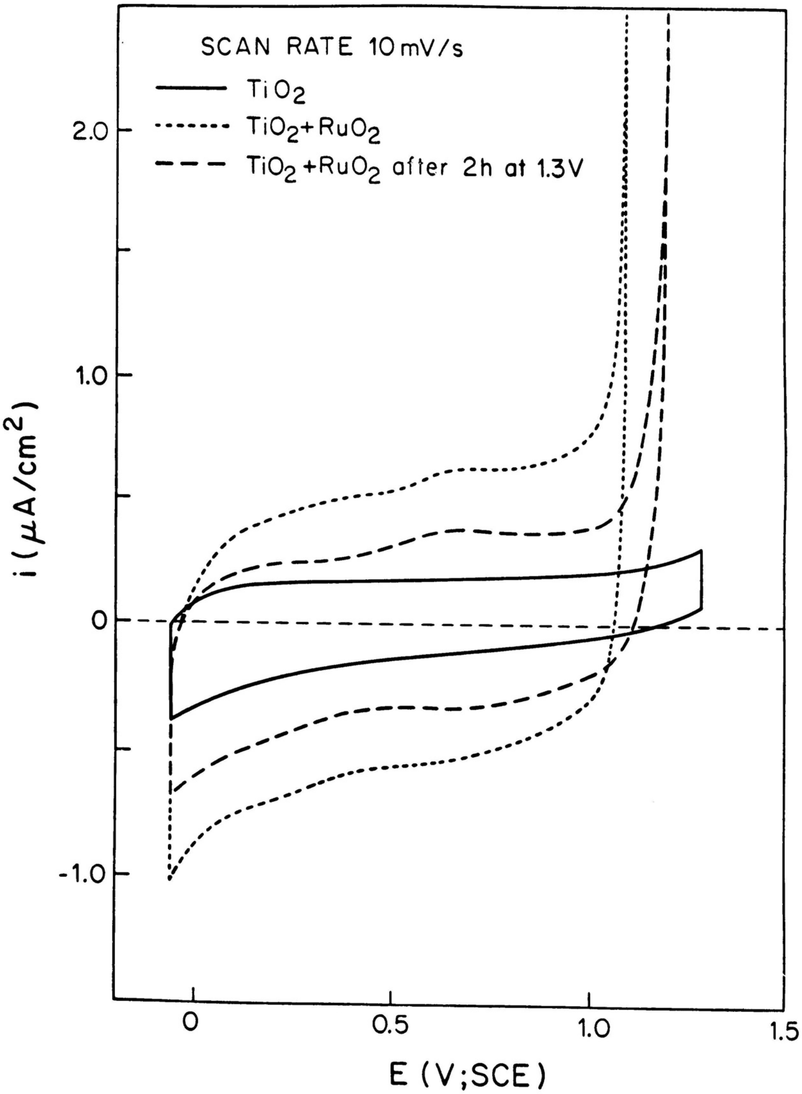


Figure 11. Cyclic voltammograms exhibiting the electrocatalytic effect of nominal one monolayer of thermally applied $RuO_2$ on the surface of titanium oxide; $TiO_2$ film grown to 3.5 V at potential ramping rate of 0.1 mV/s; $RuO_2$ applied from $RuCl_3$ at 400 °C in air; electrolyte: 0.05 M $H_2SO_4$.

### 3. THERMAL $RuO_2||TiO_2$ ANODIC FILM INTERFACE

*$RuO_2$ modification of $TiO_2$ anodic thin films.*[1,4,7] The dependence of anodic titanium oxide properties on the oxide growth rate was exploited in order to determine which structures provide the most suitable surfaces for interaction with $RuO_2$. The electrochemistry and photoelectrochemistry of nominal one monolayer coverages of $RuO_2$ deposited by thermal decomposition of $RuCl_3$ on anodically grown $TiO_2$ films were studied (lowest reported quantity applied in this way).

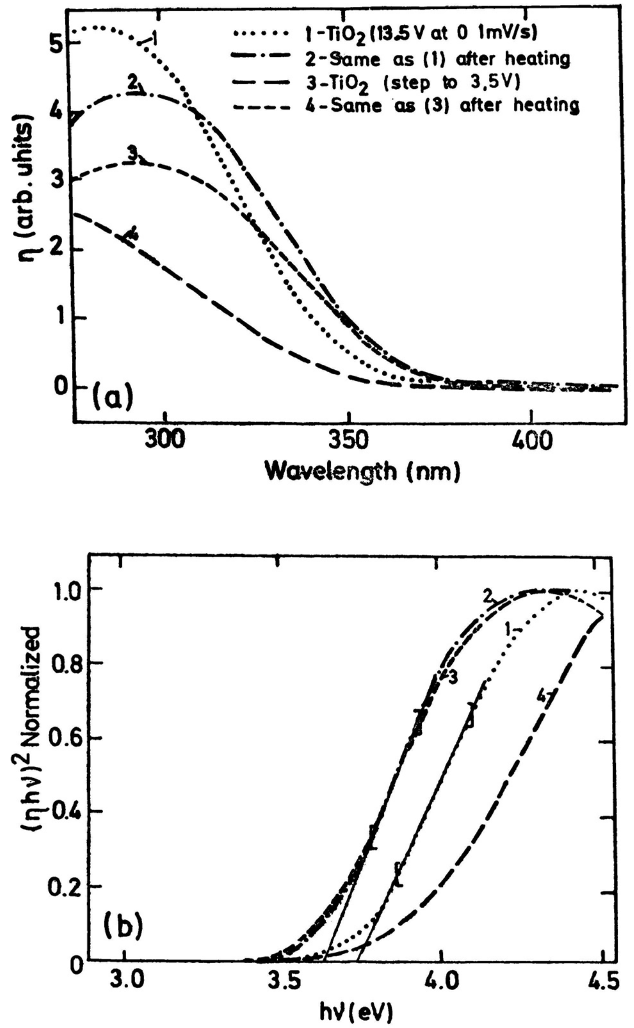


Figure 12. (a) Photospectroscopy data for anodic $TiO_2$ films at different stages of the modification by nominal one monolayer of thermally applied $RuO_2$; $TiO_2$ film grown to 3.5 V; electrode potential bias: 1 V (SCE); electrolyte: 0.05 M $H_2SO_4$; (b) Direct bandgap plots; (c) Indirect bandgap plots (see Figure 2).

*Fig. 12. to be continued*

Fig. 12. continued

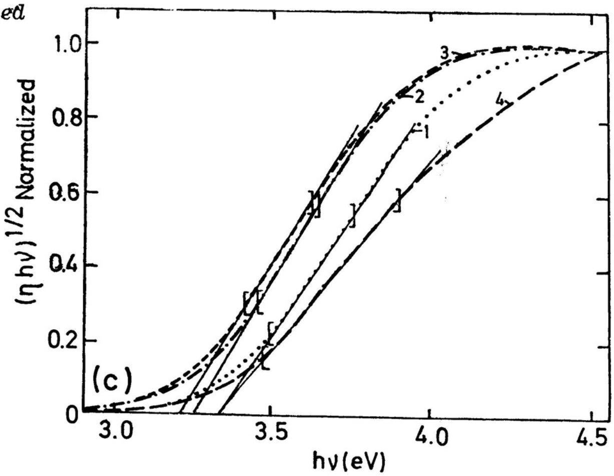


Figure 12 (c)

Three possibilities for incorporation of the applied $RuO_2$ can be considered (Figure 10). As shown in the previous section, the interaction between $RuO_2$ and $TiO_2$ occurs at their interface. Hence, in spite of the virtual isomorphism between $RuO_2$ and rutile $TiO_2$ there is no formation of solid solution.

$RuO_2$ species applied to the surface of the titanium oxide grown at potential ramping rates of 0.1 mV/s film exhibited a large and steady electrocatalytic effect (Figure 11). However, at the $TiO_2$ films grown by potential step polarization, $RuO_2$ was leaving the surface at a pace which did not allow any steady measurements. The analysis of the polarization change and the charge associated with $RuO_2$ showed that approximately 40% of the applied $RuO_2$ was incorporated along $TiO_2$ grain boundaries. This assumption is further supported by the finding that the presence of the applied $RuO_2$ at the beginning lowered the photoresponse of the system (Figure 12). Latter on when the electrocatalytic activity was decreased, the remained $RuO_2$ had to be confined along the grain boundaries in the film in order not to have an effect on the photocurrent. An explanation for these two effects can be found by inspecting the distribution of $RuO_2$ presented in Figure 10 (b). The surface overlayer of $RuO_2$ contributes to the electrocatalytic effect proportionally to its coverage. However, due to its conductivity, the same overlayer of $RuO_2$ acts as an extremely large recombination site for the photogenerated holes which manage to migrate to the electrode surface. Rather than being transferred to a water molecule across the double layer, the holes recombine with electrons which are conducted instantaneously through the $RuO_2$ surface overlayer. The $RuO_2$ confined within the grain boundaries in the film acts as recombination sites as well. Nevertheless, the latter has no effect on the further decrease of the photocurrent since the grain boundaries already act as recombination sites.

In light of the fact that $RuO_2$ exhibited tremendous electrocatalytic and photoelectrochemical effect on slowly grown oxide films and had none on step grown films, $RuO_2$ acted as a probe of the microstructure of $TiO_2$.

*Concluding remark.* The presence of *rutile* as the only identifiable phase of anodic $TiO_2$ films gives a direction for new insights towards the understanding of the $TiO_2$ and $RuO_2$ interaction. A similar importance can be given to the finding of epitaxy on the Ti||$TiO_2$ and $RuO_2$||Ti interfaces, both of relevance for the performance of a pratical electrocatalyst.

The results obtained for the $RuO_2$||Ti interface support the valence state interpretation of the XPS spectra *i.e.* the existence of $RuO_3$ at the $RuO_2$ surface. The disappearance of $RuO_3$ sites under the chemical attack of the vapor deposited titanium improves the quality of the LEED pattern exhibited at the interface comparing to the pure $RuO_2$.

Finally, the understanding the stability of the $RuO_2$||$TiO_2$ interface is added by the fact that there is no intermixing at this interface. The studies of evaporated titanium on single crystal $RuO_2$ and the thermal layers of $RuO_2$ on polycrystalline anodic $TiO_2$ both bring to the same conclusion.

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## SAŽETAK

### Površinska svojstva anodnih oksida od značaja za elektrokatalizu: $TiO_2$

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U radu su prikazana fotoelektrohemijska, elektrohemijska i površinska ispitivanja strukture i sastava međufaza Ti||$TiO_2$ $RuO_2$||$TiO_2$. Anodni filmovi $TiO_2$ formirani na titanskom substratu su ukazali na prisustvo rutila kao jedine identifi-

kovane faze u njima. Između titanskog substrata i anodnih filmova $TiO_2$ formiranih sporim rastom utvrđena je neka vrsta epitaksijalnog odnosa. Termički nanesen $RuO_2$ na anodne filmove deluje kao sonda za mikrostrukturu $TiO_2$. $RuO_2$ pokazuje elektrokatalitički i fotoelektrohemijski efekat na oksidnim filmovima formiranih sporim rastom dok kod filmova koji se brže formiraju ovih efekata nema. XPS i LEED ispitavanja monokristala $RuO_2$ i međufaze $Ru_2||Ti$ su pokazala da napareni film titana redukuje uvek prisutni $RuO_3$ u površinskim slojevima $RuO_2$. Pseudomorfizam rutilnog $RuO_2$ i $TiO_2$ vodi ka epitaksijalnom sređivanju površinskog sloja $TiO_2$. Strukture sređenog sloja $TiO_2$ na (100) ravni u odnosu na (110) ravan $RuO_2$ su interpretirani preko razlika u sastavu i rasporedu atomskih slojeva u $RuO_2$.