

Progress Report on DE-FG07-96-RT14725:
“Investigation of Novel Electrode Materials for Electrochemically Based
Remediation of High and Low-Level Mixed Wastes in the DOE Complex”

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This work is focused on the preparation of novel electrode materials for the degradation of toxic wastes in the DOE complex. One of the goals of this work is to characterize whether it is possible to use controlled doping of TiO_2 with species such as Nb in order to create new electrode materials that will facilitate the destruction of undesirable organics and inorganics, without light and instead only with an applied potential, in the waste tanks at the DOE sites. In the first part of this project, we have therefore spent an extensive amount of effort characterizing, as a baseline, the chemical and electrochemical behavior of TiO_2 itself, so that we can make robust comparisons to the behavior of the Nb-doped systems in subsequent work on this project. The preparation of these electrode films is being performed by Marc Anderson at Wisconsin, who is preparing a number of different stoichiometries, grain sizes, etc. for investigation of their electrochemical properties by the Lewis group at Caltech. First we report on the progress of the electrode preparation work, and then we describe progress on the electrochemical work.

INTRODUCTION

Several types of metallic supports have been coated with suspensions of various metal oxides. In this report, we describe studies in which titania has been coated on copper, aluminium, stainless steel, and titanium supports for further testing in photoelectrocatalytic systems.

EXPERIMENTAL

Reagents

All chemicals (Aldrich Chemical Co. and Fisher Scientific Co.) were used without further purification. The water was deionized using a Barnstead NANO pure UV ultrapure water system.

TiO₂ Sol Preparation and Characterization

Sol-gel processing techniques were employed to prepare three different titania sols (two aqueous-based and one alcoholic-based) for use in this study (1-2). An aqueous-based sol was prepared by mixing H₂O, titanium isopropoxide (Ti(i-OPr)₄) and conc. HNO₃ in a volume ratio of 300/24.75/2.1 with rapid stirring at room temperature. The resulting precipitate of titania was peptized by continuing to stir for 3 days until a stable suspension was obtained. This acid suspension was then dialyzed to a pH of 3.5 (3).

Another aqueous-based sol was prepared by mixing H₂O, Ti(i-OPr)₄ and conc. HNO₃, in a volume ratio of 300/30/2, with rapid stirring at room temperature: the resulting precipitate was peptized by refluxing the mixture at 80 °C for three days (3). This aqueous sol was used only to coat some samples of 304 stainless steel.

In addition, an alcohol-based sol was prepared. An alcohol exchange reaction was employed to convert Ti(i-OPr)₄ to the tertiary amyl alcohol (t-AmOH) analogue (4). The titania sol was then prepared by adding, with stirring, a solution of 0.72 ml of water in 49.28 mL of t-AmOH to a solution of 9.32 mL of Ti(t-OAm)₄ in 40.68 mL of t-AmOH at room temperature.

Xerogels of the aqueous based sol were prepared by allowing the solvent to evaporate slowly at room temperature. Porosities and surface areas of the unsupported xerogels after firing at different temperatures were determined by BET analysis of nitrogen adsorption isotherms. The particle size distribution in both sols was measured by laser light scattering (Brookhaven Instruments Corp.).

TiO₂ Thin-Film Preparation and Characterization

Plates of copper, aluminium, 304 stainless steel and titanium (Goodfellow Cambridge Limited) measuring 50x100x0.5 mm were prepared. Copper and aluminium plates were cleaned by placing them in acetone in an ultrasonic bath for 15 min. Titanium and stainless steel plates were first polished with Hope's stainless steel polish (The Hope Company, Inc., Bridgeton, MO). Then these plates were cleaned ultrasonically with acetone as explained above. The final steps in preparing the titanium plates were to dip them in hot 50 vol% hydrochloric acid for 2 min and rinse them with **MilliQ** water.

Aluminium, copper and titanium plates were dip-coated (withdrawal speed: 1.5 cm min⁻¹) with a single layer of the alcohol-based sol and fired at 450 °C for 1 h. Coated copper plates were not treated further. Coated aluminium and titanium plates were dip-coated a second time (at the same withdrawal speed) with a single layer of dialyzed aqueous-based TiO₂ sol and fired at either 300, 400 or 500 °C for 5 h. In some cases this procedure was repeated to deposit more layers of TiO₂.

Stainless steel plates were first fired at 450 °C for 2 h, in order to produce a metal oxide film that improved the adherence of the titania coating to the substrate (5). These pre-treated plates were dip-coated (same withdrawal speed) with one layer of the dialyzed aqueous-based sol and fired at either 300 or 500 °C for 2 h. In some cases this procedure was repeated to deposit more layers of TiO₂.

In order to study the inhibition of corrosion, samples of bare stainless steel were fired at 450 °C for 2 h, after which they were coated with several layers of the various titania sols and then fired at 500 °C for 5 h. One additional sample, coated with the sol that was peptized at 80 °C, was fired at 700 °C for 5 h.

The surfaces of these photoelectrodes were characterized with scanning electron microscopy (SEM), while the crystal structure of the deposited coatings was determined by X-ray diffraction (XRD) analysis of the film.

Reactor System and Auxiliary Equipment

Studies were conducted in a batch reactor system whose principal components were a borosilicate glass rectangular reactor vessel 55x66x25 mm (Vitro Corn Inc., Mountain Lakes, NJ), placed 10 cm in front of a 15 W fluorescent ultraviolet bulb (General Electric, F15T8.BLB). The reactor and the lamp were placed in a black acrylic box in order to avoid extraneous illumination. A plastic cap was placed on the reactor in order to seal it and hold three electrodes. Initially, 70 mL of test solution was put in the reactor, which allowed 25 cm² of the supported TiO₂ film to be immersed into the solution. The intensity of light striking the electrode was 1.35 mW cm⁻², as measured by a photometer (International Light Inc., Model IL 1400A). Electrical potentials in the reactor were controlled by a potentiostat (IBM, EC/225) that was connected to a counter electrode (platinum mesh 20x50 mm), a working electrode (metal-supported TiO₂ film), and a reference electrode (saturated calomel). All potentials are reported relative to that of the saturated calomel electrode.

Photoelectrocatalytic Reactions

The photoelectrocatalytic degradation of formic acid was conducted in the reactor system described above. Given potentials were applied with the three electrode system to perform photoelectrocatalytic reactions. Tests were conducted using aqueous solutions of formic acid (25 ppm as C) in 0.01 mol dm⁻³ NaCl. Oxygen was bubbled through the test solutions during all reactions. In each experiment two samples were taken at a given time; the first set of samples was obtained 15 min after the UV light was turned on (to allow the system to stabilize), while the second set of samples was obtained three hours after the UV light was turned on. In order to characterise the behaviour of the titania coatings that were placed on various metallic electrodes, two properties of these photoelectrodes were monitored. One property was the photocatalytic

activity of the electrode under set operating conditions. This property was measured by determining the percentage of degradation in each experiment as calculated from the change in the average concentration of total organic carbon (TOC) in each sample after illumination for 3 h. TOC values were measured with a TOC analyzer (Shimadzu Instruments, Model TOC 5000). A second property of interest was the stability of the photoelectrodes. This property was determined by measuring the photocatalytic activity of each photoelectrode, at least three separate times, at an applied potential of +0.5 V (vs SCE), and noting if any changes in activity occurred in the different measurements over time.

RESULTS

Stability and Activity of Copper-Supported Photoelectrodes

To date all the attempts to produce a stable coating of titania on a copper plate have been unsuccessful. It appears that a layer of CuO forms underneath the coating of titania. This layer of CuO readily delaminates during testing, resulting in the loss of the titania coating.

Stability and Activity of Aluminium-Supported Photoelectrodes

TiO₂ supported on aluminium displays photocatalytic and photoelectrocatalytic activity, but the TiO₂ coated aluminium electrodes corrode after several hours of use. Scanning electron micrographs of these photoelectrodes indicate that the TiO₂ coating is deposited uniformly on the aluminium surface before use (see Figure 1a). However, after use, much of the TiO₂ coating has delaminated from the substrate, and the substrate itself displays significant amounts of pitting and corrosion (Figure 1b). The application of a positive potential across the photoelectrodes accelerates the corrosion process and Al(III) is released to the solution. For example, when +0.30 V were applied across a TiO₂ coated aluminium electrode, 101 ppm of Al(III) were found in the solution after 12 h of treatment.

Corrosion was observed when the bare aluminium substrate was placed in contact with the test solution (25 ppm, as C, formic acid in 0.01 mol dm⁻³ NaCl) in the presence of O₂ and UV

light (Figure 1c). The corrosion of these electrodes was so severe that it could be observed visually. The extent of corrosion may be related to the test solution being treated. Less corrosion might be observed if less aggressive test solutions were employed. Thus it appears that Al-supported TiO₂ electrodes are not suitable for this application. No further studies were conducted with this system.

Stability and Activity of Stainless Steel-Supported Photoelectrodes

Photomicrographs of the surfaces of the fired 304 stainless steel plates (304 SS) before coating indicate that these surfaces are covered by numerous fine particles (ca. 100 nm diameter). The source of these particles has not been identified. They could be either material that was deposited while polishing these plates or small iron oxide particles formed on the surface. When the surface of the stainless steel is coated with an aqueous-based dialyzed sol of TiO₂, the resulting film follows the contours of the surface of the metal and covers the particles that are present on that surface. These coatings are quite thin; a coating prepared by depositing two layers of alcohol-based sol and firing at 500 °C for 5 h was less than 100 nm thick (see Figure 2).

TiO₂ supported on stainless steel electrodes has been used previously to study the purely photocatalytic degradation of formic acid and malic acid (5,6). We employed this material to study both photocatalytic and photoelectrocatalytic processes.

When the photoelectrodes prepared for this study were tested for purely photocatalytic activity (i.e. no applied potential), such activity was observed. An average of 5.5% of the initial formic acid present in the solution was degraded in a three hour period, when a photoelectrode coated with one layer of the dialyzed aqueous TiO₂ sol and fired at 300 °C was used. When an electrode with 6 layers of dialyzed aqueous TiO₂ sol that was fired at the same temperature was used, the percentage degraded in the same period was 30%. Photomicrographs of the surface indicate that no observable change occurred during these tests. In the case of an electrode coated with one layer of dialyzed aqueous TiO₂ sol and fired at 500 °C, only 1% of the initial formic acid was degraded in three hours.

However, when the same electrodes were employed as photoanodes, they were observed to corrode under applied potentials more positive than 0.0 V. The corrosion was obvious, because the oxidized iron caused the test solution to turn red-orange.

In an attempt to prevent the dissolution of the metallic substrate by isolating the stainless steel from the solution, additional samples coated with each type of the different TiO₂ sols described previously were applied. 304 SS plates were coated with 1, 2 and 3 layers of each of the sols (each plate always being coated with the same sol) and fired at 500 °C for 5 h after each layer was applied. The stability of the samples to applied positive potentials was tested by measuring current vs. applied potential. These experiments were conducted in the dark using a Teflon cell. Titania-coated stainless steel electrodes were used as working electrodes with a platinum counter electrode and SCE reference electrode. The cell was filled with a working solution of 25 ppm (as C) formic acid in 0.01 mol dm⁻² NaCl. The potential was scanned at 20 mV/s.

In all tests, a large increase in current was observed when the applied potential exceeded 50 mV, as shown in Figure 3. In addition, the surface of the electrode that was in contact with the solution looked damaged after 5 cycles from 500 mV to -500 mV. However, SEM images do not show any differences between the areas of the electrodes that contacted the test solution and the areas that were not exposed to the solution.

Figure 4 presents SEM images of the surfaces of the 304 SS electrodes either bare or coated with the different sols. Figure 4a shows the surface of a 303 SS plate that was fired at 500 °C. This figure indicates the presence of the small particles (ca 100 nm) previously described. Figure 4b is a magnification of the previous image in which some of the particles are shown.

Figure 4c shows the surface of an electrode coated with three layers of the alcohol-based sol, in which the typical particles present on the surface of the 304 SS after firing can be seen. Figure 4d is a magnification of the previous image. This view shows that the particles present on the surface (light grey) are now coated by smaller particles of TiO₂ (ca 20 nm).

Figure 4e shows the surface of an electrode coated with one layer of the dialyzed aqueous sol. This film is thin enough that particles and some scratches on the surface are visible through the film. Figure 4f is a magnification of the previous view. The particles of TiO₂ deposited from

the dialyzed aqueous sol are larger and less uniformly distributed than the particles deposited from the alcoholic sol.

Figure 4g shows the surface of an electrode coated with one layer of the aqueous sol peptized at 80 °C. In this case, the film appears to completely cover the particles on the surface. Therefore, we believe that this film is thicker than the others, which is a consequence of the higher viscosity of this sol compared with the others. In fact, this film is so thick that it delaminates from the electrode in several areas (not shown in the photograph). Figure 4h is a magnification of the previous image which shows the arrangement of the particles in this film.

One plate was coated with a layer of the aqueous sol peptized at 80 °C and fired at 700 °C for 5 h. The voltammograms obtained with this electrode were identical to that shown in Figure 2; and, after 50 cycles, the surface again appeared damaged., As can be noticed by comparing Figures 5a-d to Figure 4, this surface appears quite different than the films obtained by firing at 500 °C. The uncoated area is covered by small crystals (100-200 nm) in a compact arrangement (see Figure 5a). However, the coated areas contain relatively large structures on the surface (see Figure 5b) whose composition is mostly iron oxide, as determined by energy dispersive X-ray spectroscopy (EDX) analysis. (The particles shown in Figure 4a are too small to provide useful information using this technique.) The morphology of these structures appears to be a compact arrangement of deformed monocrystals (see Figure 5c). The presence of these iron oxide structures on the surface indicates that the TiO₂ coating cannot prevent corrosion of the iron surface during firing at 700 °C. This phenomenon was also reported by S. K. Yen in 316 SS coated with ZrO₂(7). As shown in Figure 5d, a flat area of the coated electrode appears like the uncoated area (see Figure 5a). However, this flat area still has enough TiO₂ on the surface to be detected by EDX analysis.

After several cyclic voltammograms were obtained, the surface exposed to the test solution was damaged. In Figure 5e, cracks and delamination of the surface can be observed. EDX analysis of the different areas shows that the TiO₂ film was not present in the areas of delamination, while only iron and the minor components are present inside these areas. Although further studies of titania coated stainless steel are being conducted, it does not appear that stainless steel supports will be suitable for this application.

Stability and Activity of Titanium-Supported Photoelectrodes

SEM analysis of the titanium-supported photoelectrodes shows that the surface is irregular with particles of different sizes deposited in the depressions on the surface (see Figures 6a-b). After coating, these particles remain under the film of TiO_2 (see Figures 6c-d) and are associated with the formation of cracks on the film. SEM analysis of samples pre-treated in different ways indicated that the origin of the particles was the stainless steel polish used in the first step of the pretreatment procedure. In the next samples this step was eliminated. Figure 6e shows the surface of a sample pretreated only by sonication with acetone in an ultrasonic bath for 5 h (with the bath cycled on and off for periods of 15 min) and coated first with a layer of alcohol-based sol (fired at 450 °C for 1 h) and then one layer of dialyzed aqueous-based sol (fired at 400 °C for 5 h). Notice that this second method for pretreating electrodes does not cause particles to deposit on the electrodes. However, cracks in the coating still could not be avoided. These cracks do not appear to be associated with particles deposited in surface depressions but appear to result from contraction of the coating after the firing procedure. These observations may indicate that these coatings are too thick to adhere well to the titanium electrode.

In another experiment, four plates of titanium were polished with an aqueous suspension of 0.3 μm Al_2O_3 particles. Two plates were coated with three layers of a dialyzed aqueous TiO_2 sol, after which one was fired at 300 °C for 5 h and the other at 500 °C for 5 h. One of the uncoated plates was fired at 300 °C and the other at 500 °C. The films and the surfaces were characterised by X-ray diffraction (XRD, Table 1) and SEM (Figures 7a-f).

Figures 7a and 7b show the surface of uncoated and coated samples fired at 300 °C respectively. By comparing these figures, one can conclude that the TiO_2 film covers completely the surface of the support. The coated sample exhibits a homogeneous surface with small pores and some cracks in the coating. Images of the uncoated (Figure 7c-d at different magnifications) and coated (Figures 7e-f at different magnifications) samples fired at 500 °C are also shown. Once again, the film covers completely the surface of the metal. However, after firing at 500 °C the particles of TiO_2 are well defined and bigger than when fired at 300 °C. As shown in Table I, this growth in particle size is also associated with partial conversion of anatase crystals to rutile.

Table 1 Crystal structures of the surfaces of titanium plates treated in different ways.

	Fired at 300 °C	Fired at 500 °C
Uncoated	No Crystalline Phase	Rutile
Coated	Anatase	Anatase + Rutile

TiO₂ supported on titanium displays both photoelectrocatalytic activity and reasonable stability. Figure 8 shows the average activity of individual photoelectrodes that were fired at different temperatures, with the error bars representing the relative standard deviation observed in either three or four tests of each electrode. While the electrode that was fired at 300 °C was not the most active, it did display the best reproducibility. Figure 9 indicates the variation in behaviour that was observed for this electrode.

On the other hand, for the electrode that was fired at 500 °C, a continuous diminution in its catalytic activity was noticed as each of the three tests was conducted. After the tests were completed, photomicrographs of the photoelectrodes fired at 500 °C indicated that in some areas the film of TiO₂ had separated from the substrate. The lack of contact between the titania coating and the conductive substrate may contribute to the decreased activity of this photoelectrode. However, the current that passes through the reactor is higher for the electrode fired at 500 °C (2.8-3.5 mA) than for the electrode fired at 300 °C (1.6-2.0 mA). In addition, it appears that the particles in the titania coating fired at 500 °C are larger than the particles in the titania coating fired at 300 °C. Thus, the larger particles improve the conductivity of the photoelectrodes. This behaviour is not surprising. As the porous coatings are heated, grain growth will occur. As the particle size increases, the number of grain boundaries decreases. Because each grain boundary resists the passage of current, the conductivity of the coatings, and thus of the photoelectrodes, should increase with increasing firing temperature.

However, coatings that contain larger particles do not display improved catalytic activity. In addition to the possible delamination of the TiO_2 film mentioned above, two other factors may also contribute to this behaviour. i) XRD analysis of the films indicates that the crystal structure of the films fired at 300 °C is that of the anatase form of titania, while the films fired at 500 °C are a mixture of anatase and rutile. Results from several photocatalytic studies have suggested that rutile is the less photoactive form of titania (for example see ref 8). ii) Firing these porous coatings at higher temperatures reduces their surface area. Thus less catalyst will contact the test solution in the coatings that were fired at 500 °C. Both of these factors would offset the improvement in conductivity that is obtained by firing the coatings at 500 °C.

Because the titania-coated titanium electrodes displayed reasonably reproducible behaviour in these initial tests (as opposed to the significant degradation of the other substrates that was observed), further tests of the photocatalytic and photoelectrocatalytic properties of these titanium-supported photoelectrodes were conducted. These additional tests are described in the next section, using coatings of titania deposited from dialyzed aqueous sols.

Effect of Different Variables on the Behaviour of the Titanium-Supported Photoelectrodes

a) Effect of the Applied Potential

The effect of the applied potential on the removal of formic acid using photoelectrodes fired at different temperatures (i.e., the photoelectrocatalytic process) is shown in Figures 10a and 10b. We believe that these results correspond to the photoelectrochemical process because the pure electrochemical oxidation of formic acid on TiO_2 films deposited on conductive glass occurs only at potentials higher than 2 V (9) and on uncoated titanium at potentials higher than 3 V (this work).

Inspection of Figures 10a and 10b indicates that, for films fired at both 300 and 500 °C, the degradation of formic acid is highest for applied potentials of +1.0 V. However, only a small improvement in degradation ability is obtained by increasing the applied potential from +0.5 to +1.0 V. Therefore further studies were conducted under an applied potential of +0.5 V.

b) Effect of the Number of Layers of TiO₂

Photoelectrodes containing various numbers of layers of dialyzed aqueous TiO₂ were fabricated. Figure 11 shows the activity of these photoelectrodes after being used for three hours of treatment. The amount of formic acid degraded is roughly proportional to the amount of TiO₂ deposited on the substrate (see Figure 12). The data shown in Figure 11 demonstrate several trends. 1) Application of a potential of +0.5 V across the titania coating significantly increases the activity of the photoelectrode above that observed when no potential is applied. 2) With a potential of +0.5 V applied across the photoelectrode, only a relatively small improvement in the activity of the photoelectrode is observed when more than two layers of titania are present. 3) Application of a potential across the titania coating has only a small effect when the coating consists of 10 layers of titania. Fluctuations in the amount degraded with different numbers of layers were reported previously in experiments that employed TiO₂ supported on conductive glass photoelectrodes (10). These fluctuations were attributed to experimental variations.

The first observation can be explained readily. When titania is illuminated by band gap radiation, electron-hole pairs are generated that are responsible for the photocatalytic activity of the material. By applying a potential across the photoactive titania, recombination of photogenerated electron-hole pairs is minimised. As a result the activity of the titania increases. Note that other factors may well contribute to this phenomenon which has been reported by several researchers (1-6). There is also an obvious explanation for the other two observations reported above. Because titania is a poor conductor of electrical current, the thicker coatings of titania that are formed by depositing more layers of titania on the substrate are likely to inhibit the effectiveness of the applied electric field. In these experiments, though, a second factor may well contribute. If the degradation of formic acid follows first order kinetics, then the removal of additional formic acid beyond the 60% removed by two layers of TiO₂ may proceed slowly. These experiments were not conducted in a manner that would allow these two possibilities to be distinguished.

The activity of multilayer photoelectrodes was observed to decrease with the number of times that they were used. For example, when the photoelectrode that was coated with 4 layers of titania was employed in three successive tests, the activity of the photoelectrode decreased by 22% as these tests were conducted. SEM analysis of this photoelectrode indicates that the

diminution in its activity could not be associated with delamination of the TiO_2 layer. However, the mass of the photoelectrode was found to decrease by 0.9 mg after it was used three times. Therefore, it appears that the stability of titanium-supported photoelectrodes that contain multiple layers of titania is questionable.

c) Effect of the Concentration of NaCl

Figure 13 shows the effect of different concentrations of NaCl in solution on the activity of the titanium-supported TiO_2 coated photoelectrodes. The presence of NaCl seems to decrease the rate of degradation of formic acid in the pure photochemical process. This phenomenon was reported previously in studies of photocatalysis (17) and in a study of photoelectrocatalysis that employed titania photoelectrodes coated on conductive glass (10). Lowered efficiencies in photocatalytic reactions with increasing ionic strength are likely attributable to the competition between the formate ion and electrostatically adsorbed ionic species at the TiO_2 surface. Application of a positive potential not only improves the activity of the titania photocatalyst but also minimises the effect of the added NaCl. At present the reason for this improved performance is not clear.

SUMMARY

TiO_2 supported on metals displays photocatalytic and photoelectrocatalytic activity, but the stability of the photoelectrodes depends on the stability of the metal against corrosion. In spite of the efforts made to date, films of TiO_2 can not prevent the corrosion of copper, aluminium or stainless steel. Such corrosion may also occur on TiO_2 coated titanium electrodes, but this possibility has not been proven. TiO_2 coated titanium electrodes have been shown to display reproducible behavior with repeated use in photoelectrocatalytic processes. Thus, this system has been studied most extensively for this project.

Purely photocatalytic activity seems to vary with the support. For example, the photoactivity of TiO_2 supported on stainless steel is lower than the photoactivity of TiO_2 supported on titanium or aluminium. However, exposure of TiO_2 coated aluminium electrodes to near UV light and a saline solution of formic acid causes severe corrosion of these electrodes.

Application of positive potentials across TiO₂ films supported on titanium improves the efficiency of the photocatalytic process. This behaviour is the same as previously reported with TiO₂ supported on conductive glass. Firing temperature plays an important role in determining the electrochemical behaviour of the electrodes. The intensity of the current in the system (under otherwise identical conditions) increases with the firing temperature, although no corresponding improvement in the catalytic activity was detected. Catalytic activity of these electrodes can be increased by applying multiple coatings of TiO₂ to the titanium electrode. However, more studies are necessary in order to improve the adherence of multilayer TiO₂ electrodes with repeated use. We expect to find an optimal thickness for the film of TiO₂ that provides maximum photocatalytic activity with the minimum amount of TiO₂ when a positive potential is applied across the electrode.

The application of positive potentials across TiO₂ films diminishes the adverse effect of salt in solution on the photocatalytic activity of the system. This result is very interesting because most aqueous wastes that could be purified using this technology contain some salt.

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FIGURE CAPTIONS

Figure 1. Scanning electron photomicrographs of aluminium photoelectrodes fired at 500 °C and treated in different ways. a) Titania coated electrode prepared as described in the text (see p. 2) before exposure to the test solution. b) Same electrode as (a) after 7 h exposure to the test solution and UV light with pure oxygen bubbled through the solution. c) Uncoated electrode after 8 h exposure to the test solution and UV light with pure oxygen bubbled through the solution.

Figure 2. Scanning electron photomicrograph of a 304 stainless steel-supported titania photoelectrode. The coating is the narrow band across the center of the figure that is labeled 79.4 nm. The relatively uniform grayish area below the coating is the stainless steel electrode, while the region above the coating is a layer of resin used to prepare the specimen.

Figure 3. Current-potential plot for a stainless steel-supported titania photoelectrode that was coated with 3 layers of alcohol-based titania sol and fired at 500 °C for 5 h.

Figure 4. Scanning electron photomicrographs of stainless steel photoelectrodes prepared in different ways. All samples were initially fired at 450 °C for 2 h. a) Uncoated electrode fired a second time at 500 °C for 5 h. b) Same as (a) but at higher magnification. c) Electrode coated with 3 layers of alcohol-based titania sol and fired at 500 °C for 5 h. d) Same as (c) but at higher magnification. e) Electrode coated with 1 layer of dialyzed aqueous-based titania sol and fired at 500 °C for 5 h. f) Same as (e) but at higher magnification. g) Electrode coated with 1 layer of peptized (80 °C) aqueous-based titania sol and fired at 500 °C for 5 h. h) Same as (g) but at higher magnification.

Figure 5. Scanning electron photomicrographs of stainless steel photoelectrodes. All samples were initially fired at 450 °C for 2 h. a) Uncoated electrode fired a second time at 700 °C for 5 h. b) Electrode coated with 1 layer of peptized titania sol and fired at 700 °C for 5 h. c) Magnification of the main feature shown in (b). cl) Magnification of a flat area shown in (b). e)

Coated surface prepared as in (b) after 50 cyclic voltammograms (-0.5 V to +0.5 V at a scan rate of 20 mV/sec).

Figure 6. Scanning electron photomicrographs of titanium photoelectrodes prepared in different ways. a) Uncoated electrode pretreated as described in the text (see p. 2). b) Same as (a) but at higher magnification. c) Electrode coated with 1 layer of alcohol-based titania sol, fired at 450 °C for 1 h, coated again with 1 layer of dialyzed titania sol, and fired at 300 °C for 5 h. d) Same as (c) but at higher magnification. e) Electrode coated and fired as described in the text. Unlike the electrode shown in (a-d), this electrode has not been polished.

Figure 7. Scanning electron photomicrographs of titanium electrodes prepared in different ways. a) Uncoated electrode polished with alumina and fired at 300 °C for 5 h. b) Polished electrode coated with 3 layers of dialyzed titania sol and fired at 300 °C for 5 h. c) Uncoated electrode polished with alumina and fired at 500 °C for 5 h. d) Same as (c) but at higher magnification. e) Polished electrode coated with 3 layers of dialyzed titania sol and fired at 500 °C for 5 h. f) Same as (e) but at higher magnification.

Figure 8. Effect of firing temperature on the photoelectrocatalytic activity of titanium-supported titania photoelectrodes. Electrodes were prepared by polishing titanium plates with stainless steel polish, coating with 1 layer of alcohol-based sol, firing at 450 °C for 1 h, coating with 1 layer of dialyzed titania sol, and firing at the indicated temperature for 5 h. Activity of the electrodes was measured as described in the text (see p. 3) with an applied potential of +0.5 V. The percent of formic acid remaining in solution corresponds to the average of at least three separate tests.

Figure 9. Variation in activity of the titanium-supported titania photoelectrode that was fired at 300 °C.

Figure 10. Effect of applied potential on the removal of formic acid. a) Electrode prepared as described in Figure 8 and fired at 300 °C for 5 h. b) Electrode prepared as described in Figure 8 and fired at 500 °C for 5 h.

Figure 11. Activity of photoelectrodes both with and without an applied potential as a function of the number of layers of dialyzed titania sol applied to the electrode. All electrodes were first coated with 1 layer of alcohol-based titania sol and fired at 450 °C for 1 h. After the indicated number of coatings with the dialyzed sol, all electrodes were fired at 300 °C for 5 h.

Figure 12. Amount of titania deposited on the titanium support as a function of the number of layers of titania applied. Layer 1 includes the mass of both one coating of alcohol-based titania sol fired at 450 °C and one coating of dialyzed aqueous-based titania sol fired at 300 °C. Additional layers include the mass deposited from additional coatings of the dialyzed sol fired at 300 °C.

Figure 13. Effect of applied potential and salt concentration in the test solution on the activity of titania photoelectrodes. All electrodes were prepared by polishing titanium plates with stainless steel polish, coating with 1 layer of alcohol-based titania sol, firing at 450 °C for 1 h, coating with 1 layer of dialyzed titania sol, and firing at 300 °C for 5 h. (NAP = no applied potential).

Figure 1

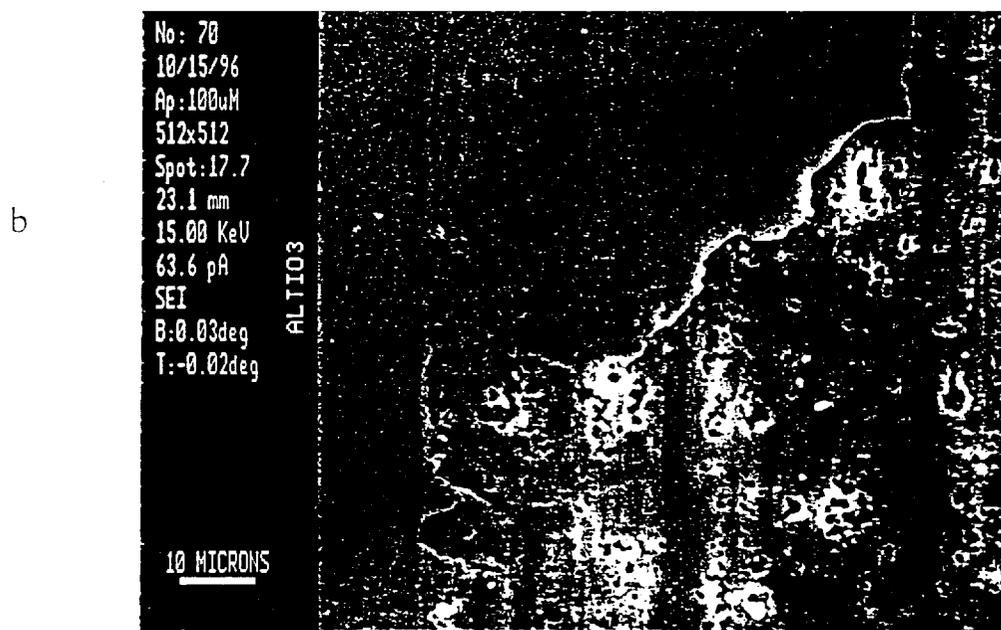
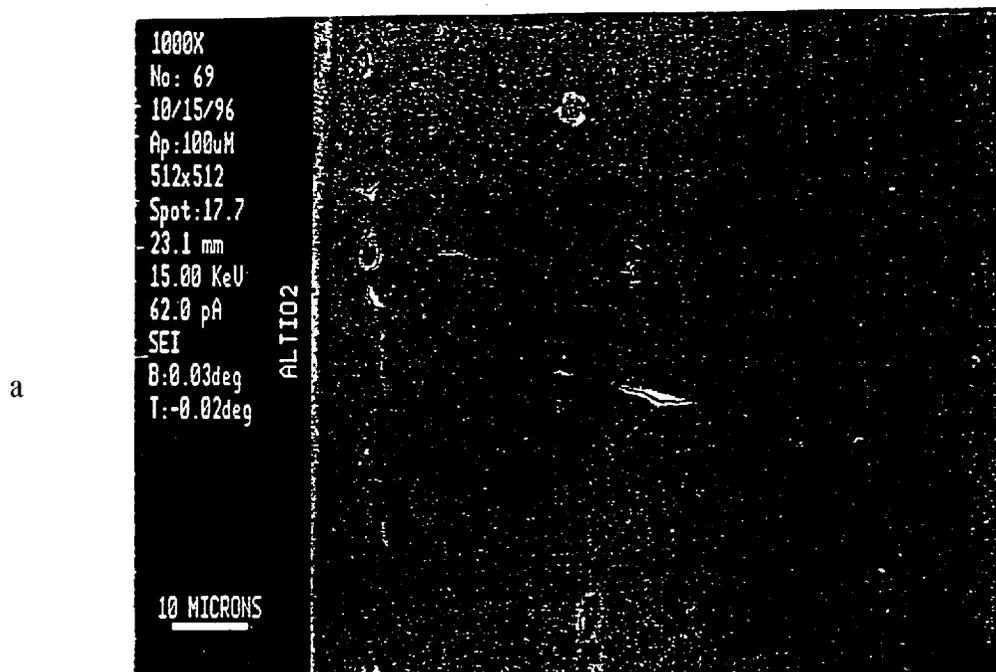


Figure 1 (continuation)



Figure 2

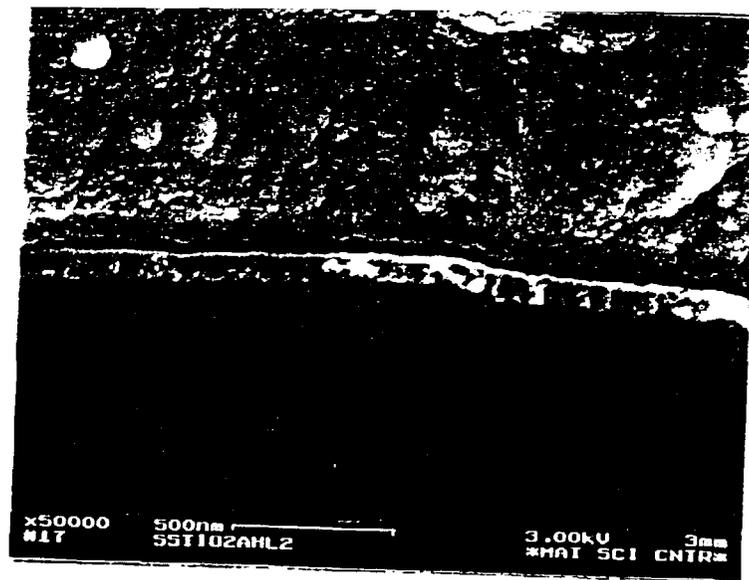


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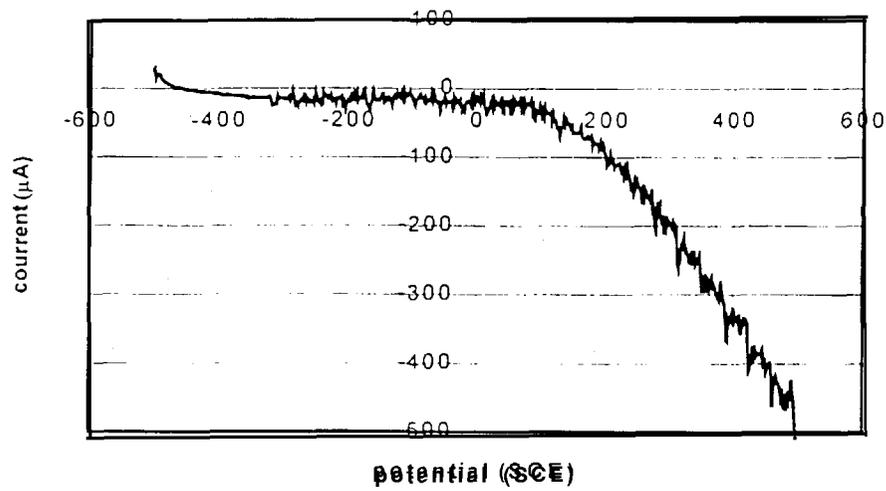
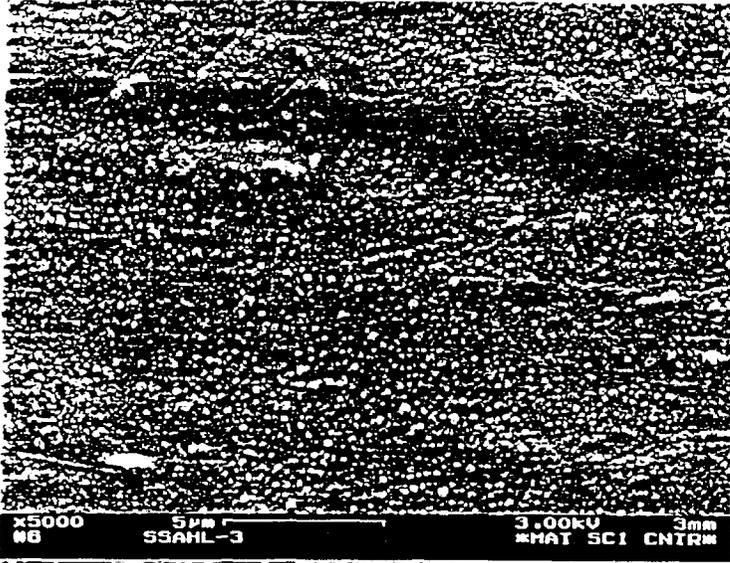
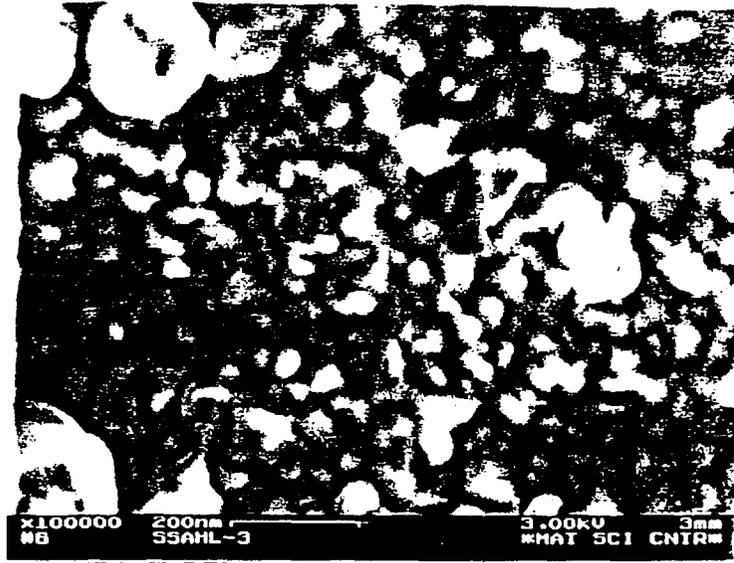


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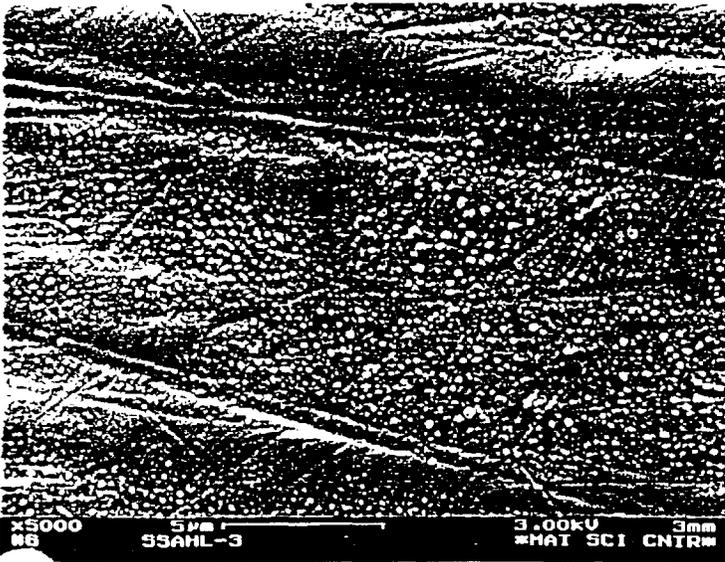
a



b



c



d

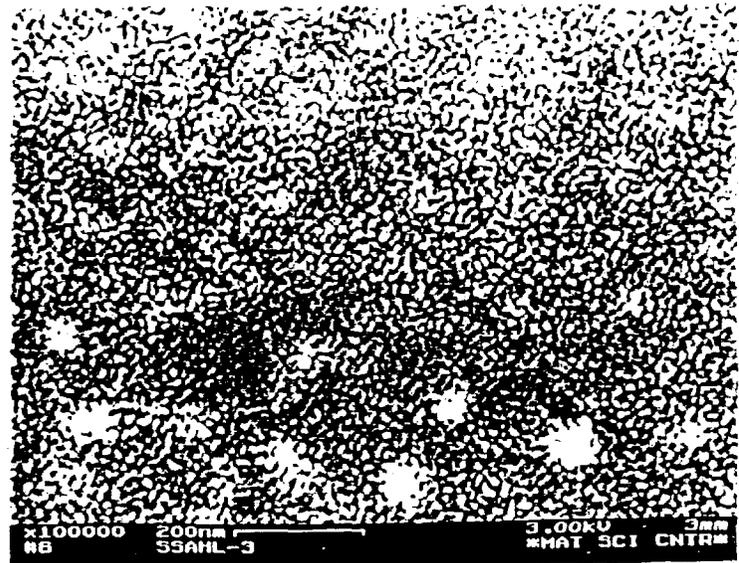


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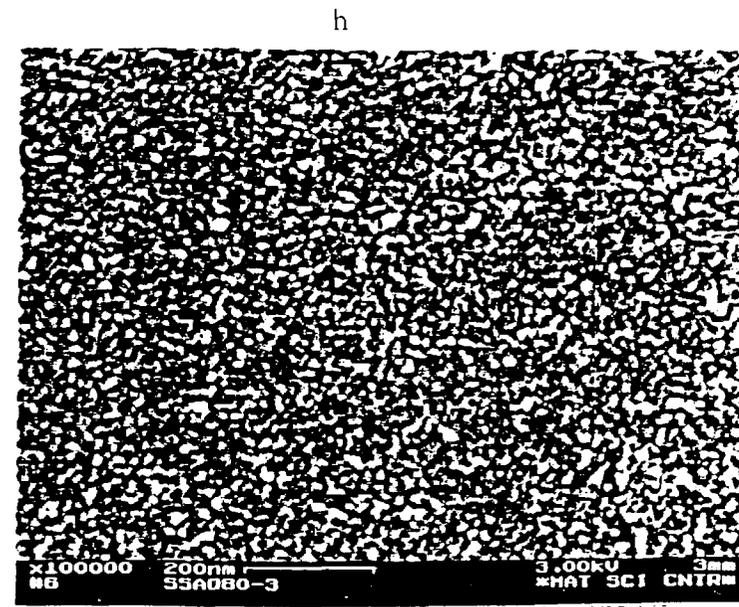
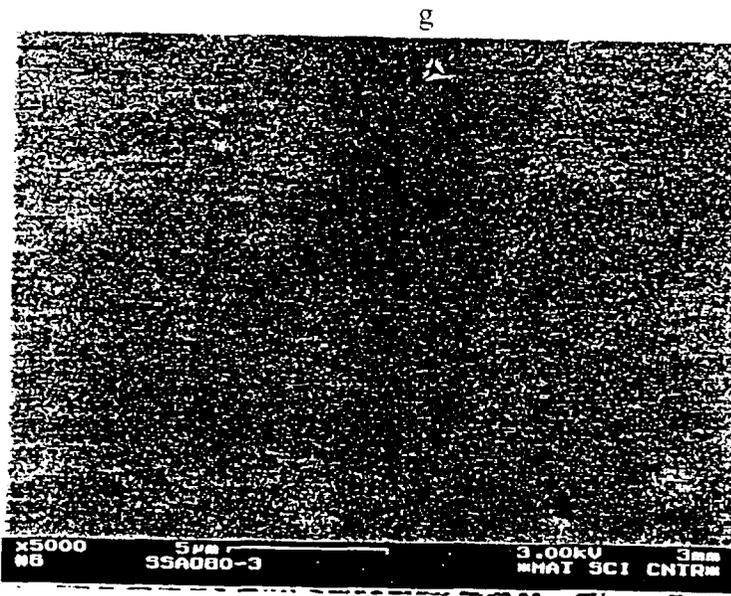
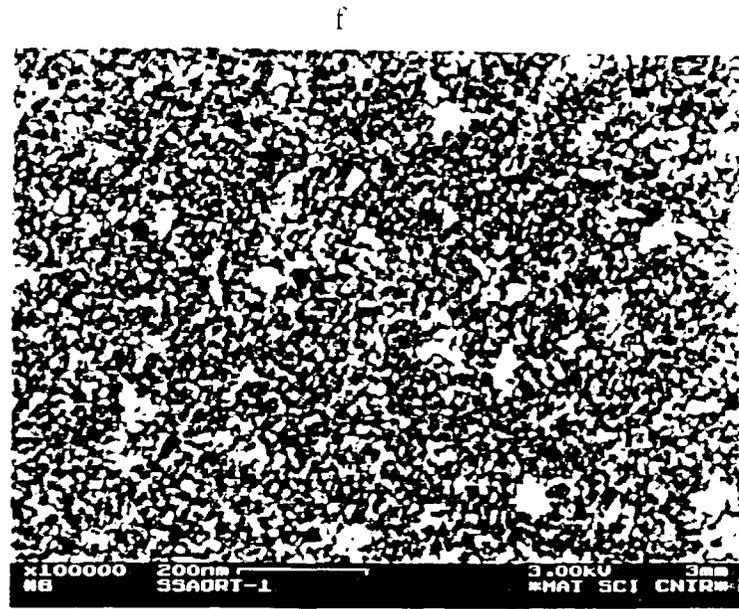
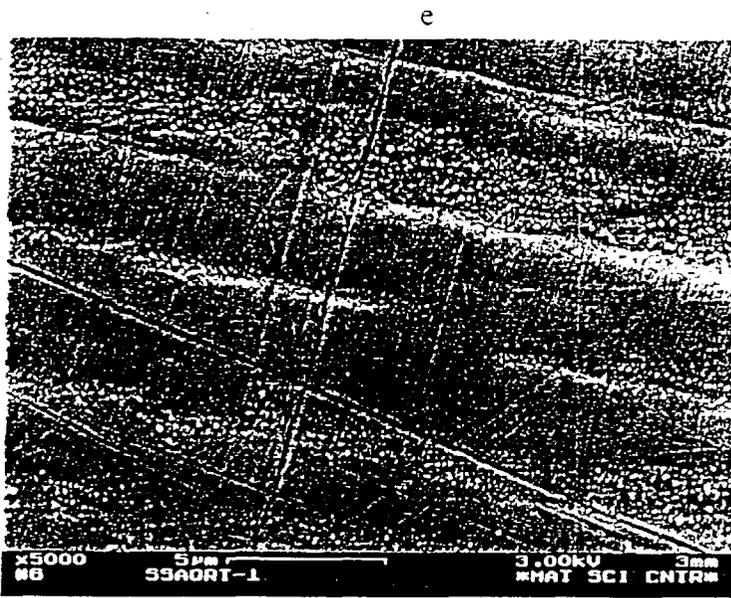


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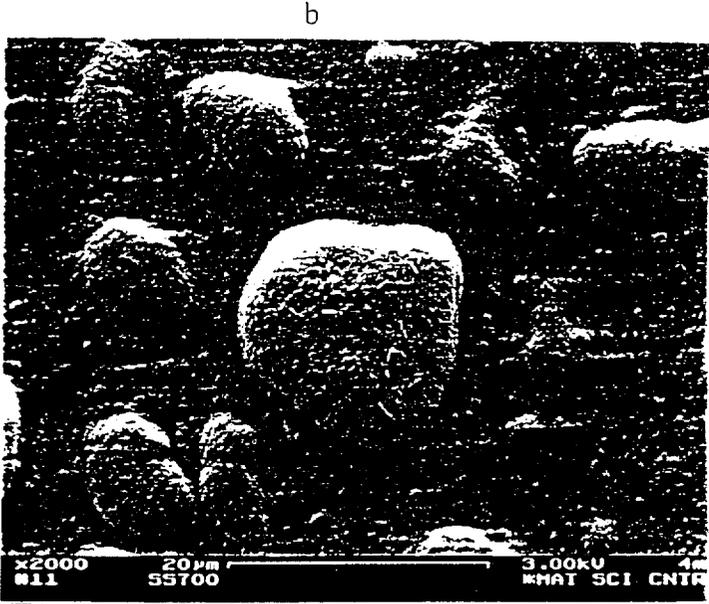


Figure 5 (continuation)

e

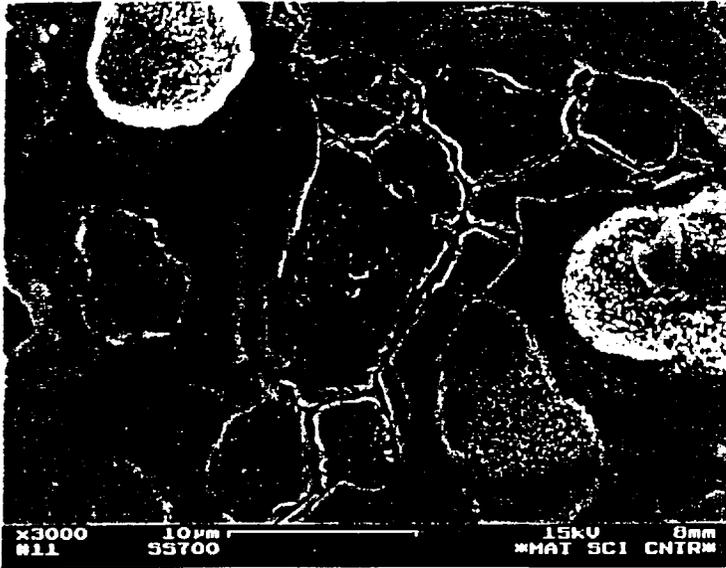


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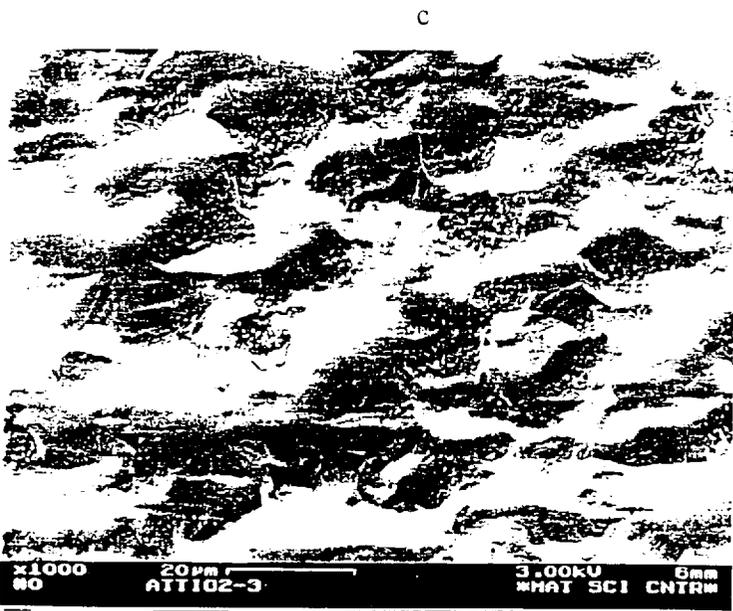
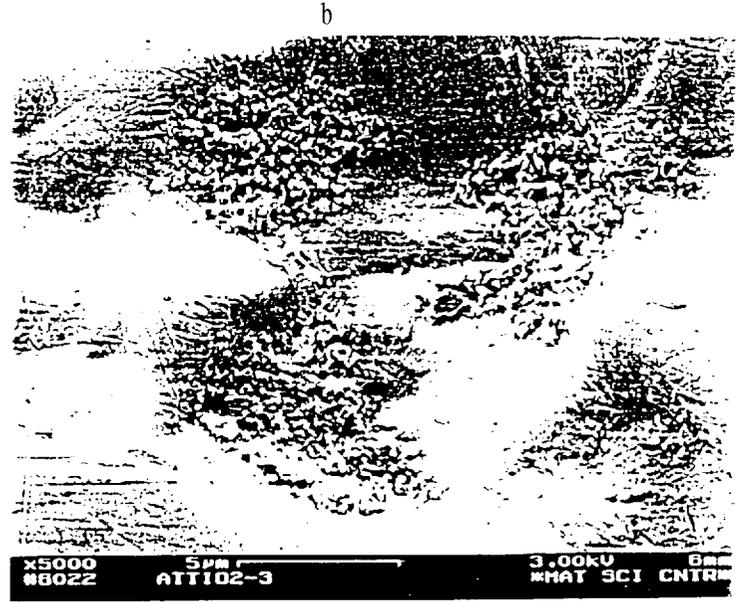
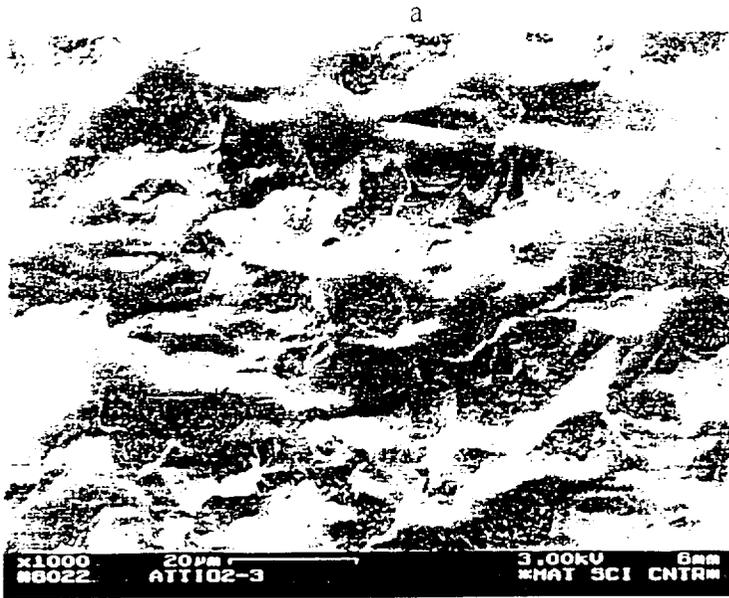


Figure6 (continuation)

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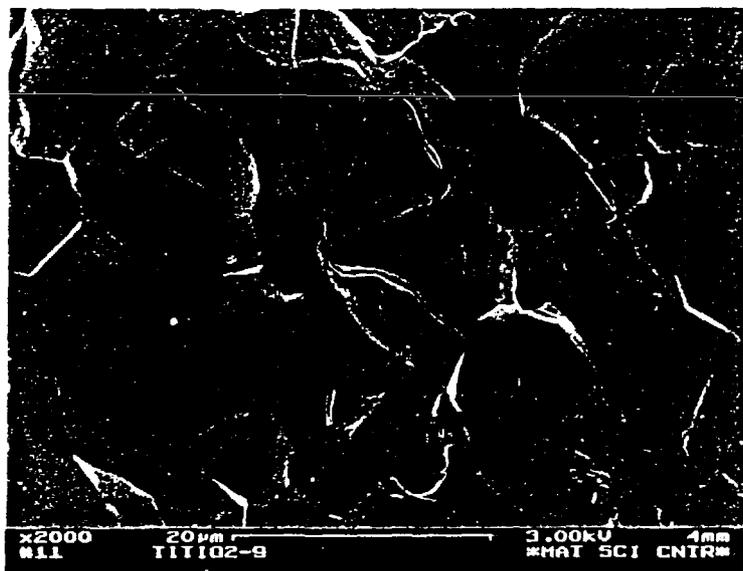


Figure 7

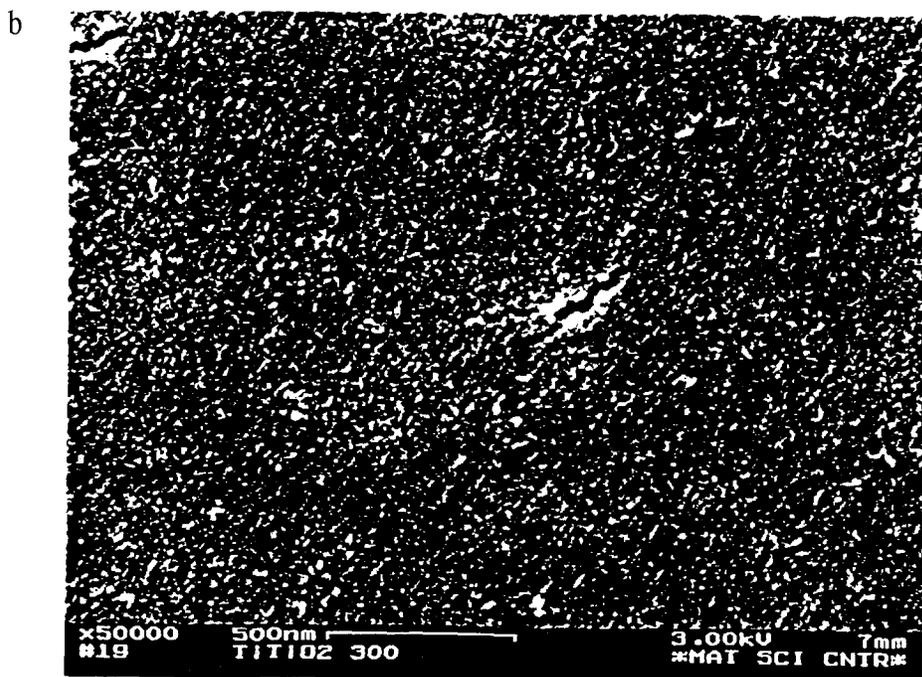
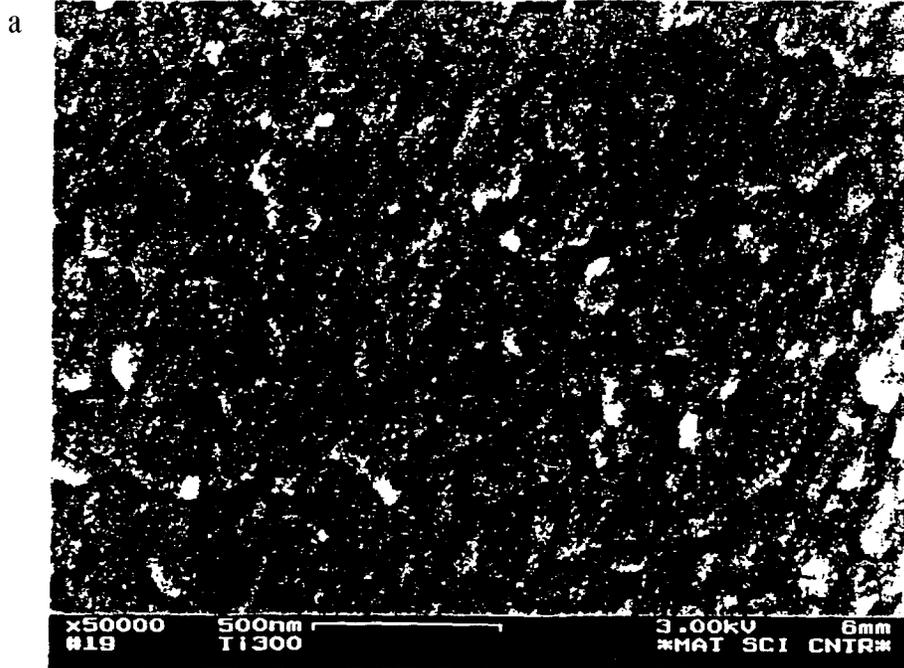
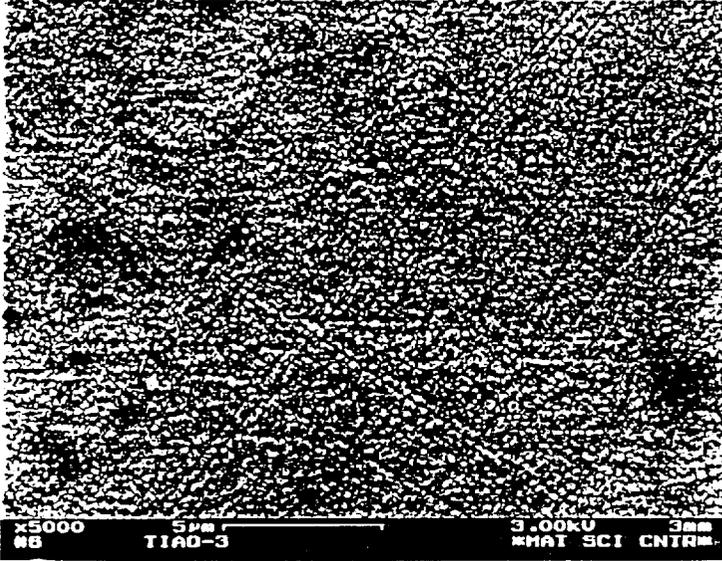
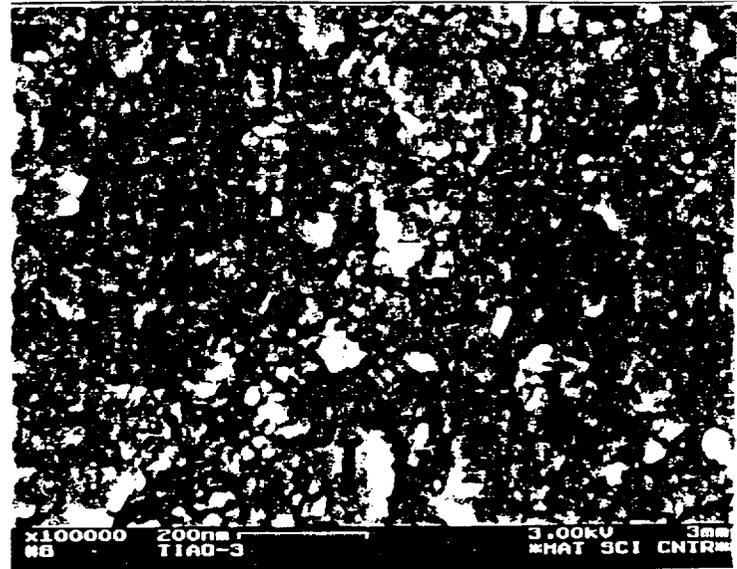


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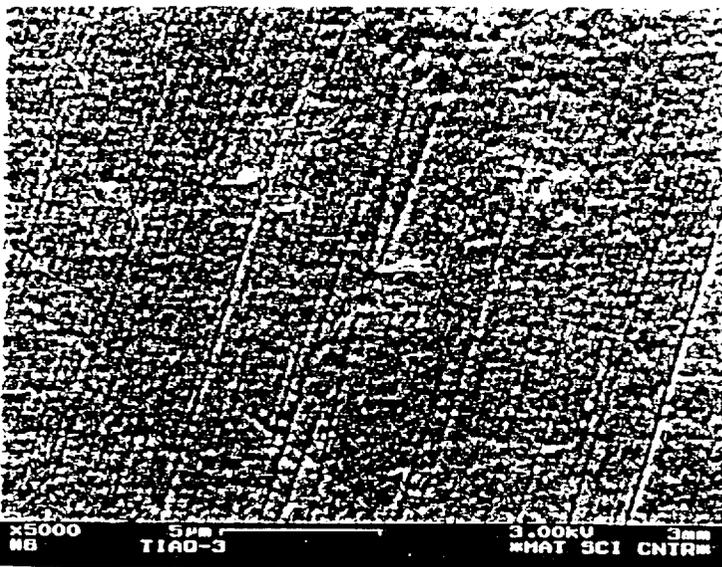
c



d



e



f

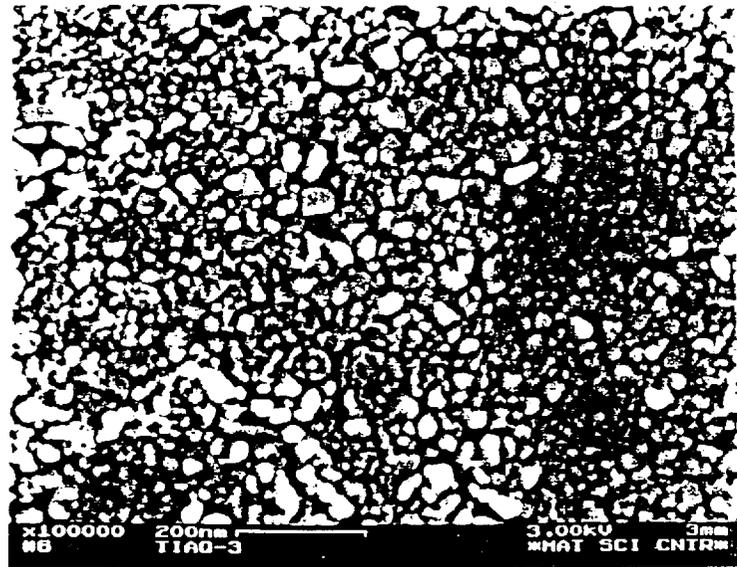


Figure 8

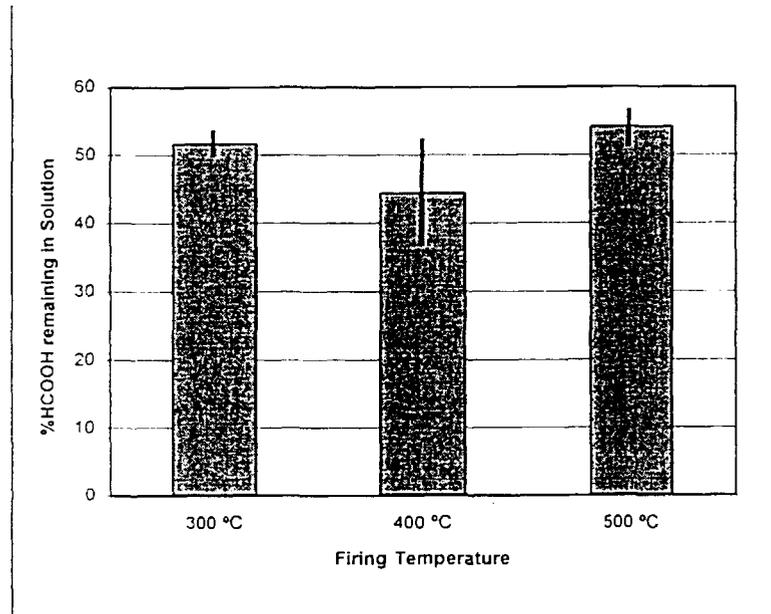


Figure 9

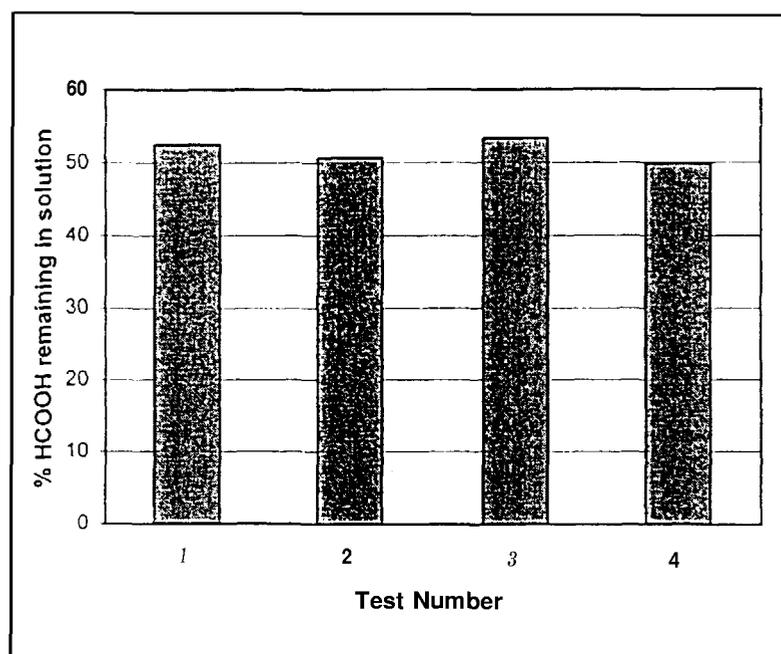


Figure 10

a

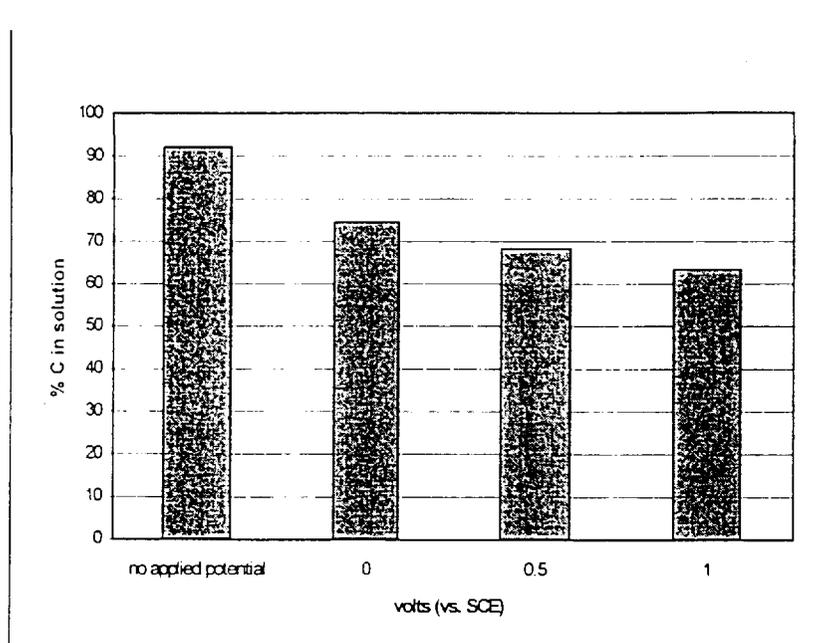
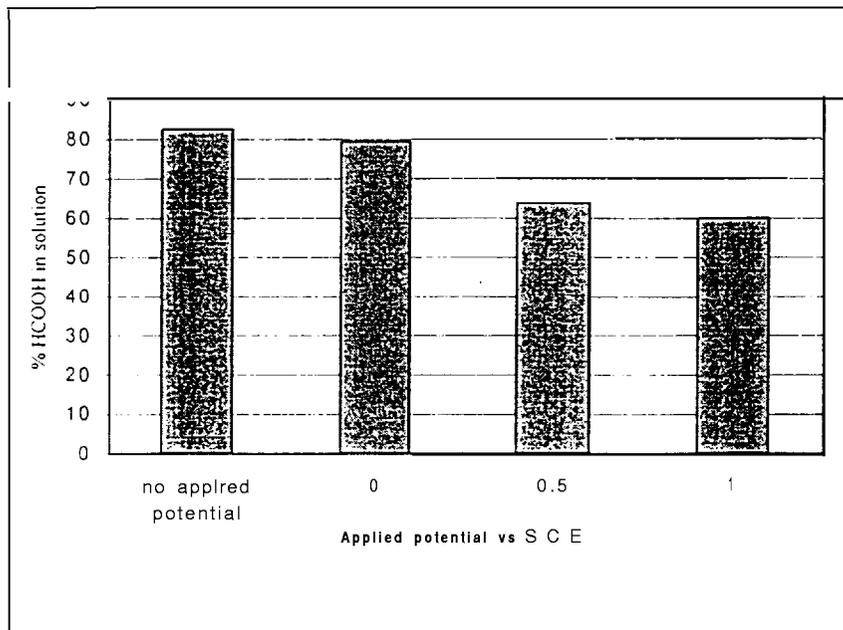


Figure 11

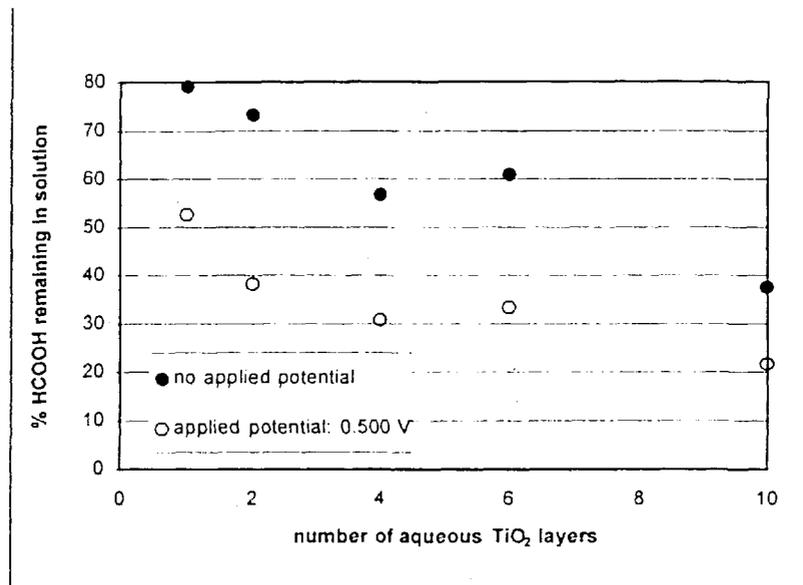


Figure 12

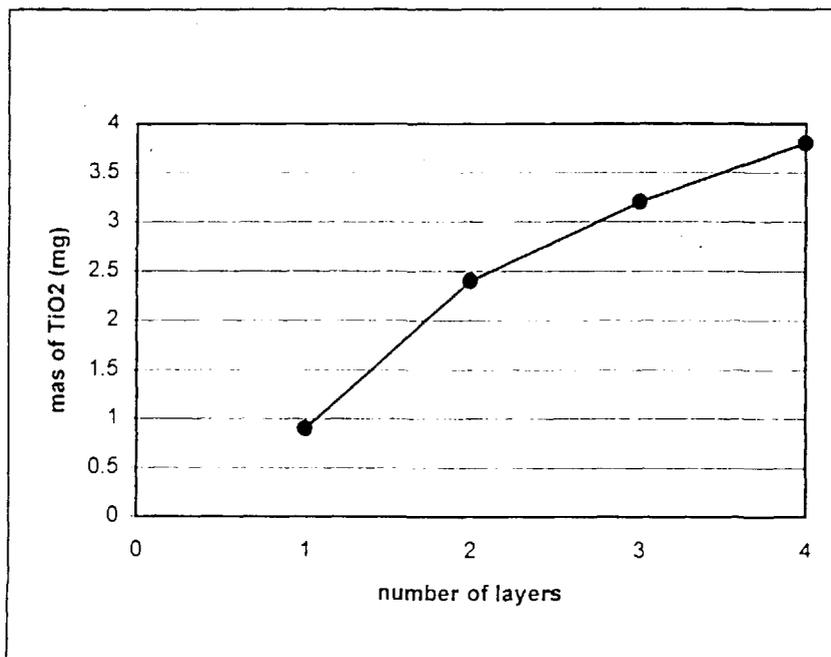
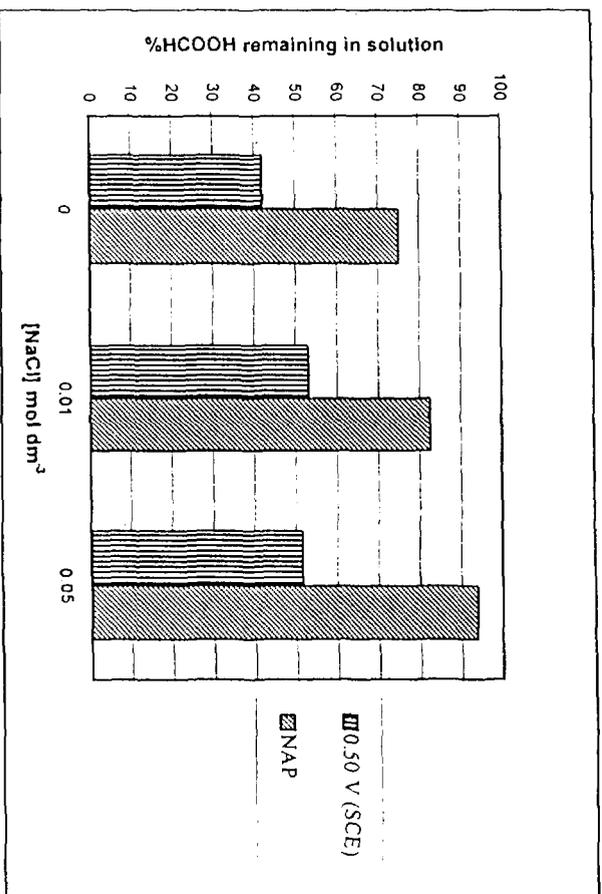


Figure 13



Electrochemical Studies

Electrodes were characterized both in the dark, to determine their baseline electrochemical properties, and in the light with adsorbed dyes, in order to determine their trap state density and other properties that will be important in ultimately affecting the performance of these systems in an electrochemical cell. These studies are described briefly below.

Electrodes were prepared by first depositing a layer of TiCl_4 in isopropanol onto 3 mm thick glass coated with a conducting layer of F-doped SnO_2 (manufact.). The layer was evenly spread by pulling a glass slide across the surface of the electrode, where Scotch tape on either side of the electrode region acted as a spacer for the slide. After the isopropanol had evaporated, the colloid solution was spread onto the conducting glass in a similar fashion. Once this layer had dried, the electrodes were fired in a tube furnace under flowing air at 450 °C for 30 minutes. Once the electrodes had cooled, 100 mL of a freshly made solution of 0.2 M TiCl_4 in water was deposited on each electrode. After the electrodes were covered and allowed to sit overnight, the electrodes were rinsed with isopropanol. Sample electrode thicknesses were approximately 5 μm as measured by profilometry.

Initial experiments with TiO_2 electrodes showed poor reproducibility. It was hypothesized that variables such as water concentration and solution pH were affecting the current-voltage behavior of these electrodes, so care was taken to control these variables. All reagents and solutions listed above were stored in a nitrogen-purged box after purification. The pyridinium triflate and pyridinium were added to both the dye and electrolyte solutions in 0.001 M concentrations to maintain a constant initial pH. In pH studies, these buffered solutions were made more basic by adding Proton Sponge. Enough Proton Sponge was added so that the pyridine/pyridinium could no longer act as a buffer. All cells were constructed inside the nitrogen-purged box and sealed to avoid water contamination before being brought out of the box. These precautions led to greatly improved reproducibility.

Current density vs potential experiments were performed using an EG&G Princeton Applied Research (PAR) Model 362 Potential Controller in conjunction with a Houston Instrument Omnigraphic 2000 recorder. Light intensities were controlled by the use of an ELH W-halogen bulb and were determined by use of a calibrated silicon photodiode (Solarex). A UV filter was used to avoid direct excitation of electrons in the titanium dioxide. All measurements were performed in a three-electrode potentiostatic set-up, with a Pt wire reference and Pt gauze counter electrode. The distance between the working and counter electrodes was approximately 2 mm and no stirring was performed.

Some dye-electrolyte combinations were found to require some equilibration time to reach a stable open-circuit voltage: therefore, all cells were allowed to equilibrate for at least 30 minutes after exposure to a new solution before data published here were recorded. After exposure to Proton Sponge, electrodes were allowed to reequilibrate with the buffered I/I₂ solution for at least 2 hours. Although the current-voltage properties of these junctions remained stable while the cell was assembled, once the electrodes were removed from the iodine solution they tended to degrade. For this reason, fresh electrodes were used in all experiments.

Spectral response data was obtained by biasing the cell to short circuit and measuring the voltage output from the current monitor on the potentiostat. Monochromatic light was obtained from a Spex 1682A tungsten lamp in conjunction with a Spex 1681 B monochromator with 1.25 mm slits. For the TiO₂ electrodes, the dark current tended to drift slightly over time, so the dark current was measured at each wavelength and subtracted from the photocurrent at that wavelength. The light intensity from a beam-split portion of the monochromator output was measured by monitoring the photocurrent at a Si photodiode from United Detector Technology. This diode thus served as a calibration of the lamp intensity. Quantum yields were obtained by placing a calibrated Si photodiode in the same position as the TiO₂ working electrode and measuring the photocurrent at short circuit, then correcting the data from the TiO₂. Current-voltage data at 1 Sun illumination was obtained

before and after each run. Electrodes which showed significant decreases in photocurrent (2-5%) were viewed to be defective and were not included in the final analysis.

III. Results:

A. Characterization of Unsensitized Electrodes

The current-voltage behavior in the dark for a nanoporous titanium dioxide electrode was first compared to the current-voltage behavior for a conducting glass electrode in a solution of LiI/I_2 . Both reduction and oxidation of the I_2/I^- couple require high over-potentials at the conducting glass electrode and very low currents are observed in either potential direction. In contrast, the TiO_2 electrode shows rectifying behavior and yields much higher dark currents in forward bias than the conducting glass alone. This behavior indicates there are slow kinetics of electron transfer for iodine at the conducting glass surface. Since the TiO_2 is capable of reducing I_2 but not of oxidizing LiI in the dark, a concentration gradient is developed which effectively separates the charge. To further support this explanation, a similar experiment was performed with $\text{Me}_2\text{Fc}^{+/0}$ as the redox couple in solution. This redox couple was chosen because the reduction potential of this couple is reasonably close to that of the I_2/I^- . In this case, very high currents were observed in both potential directions at the conducting glass electrode. At the titanium dioxide electrode, similar behavior was observed. Although data is not shown here, dye-sensitized electrodes immersed in solutions of $\text{Me}_2\text{Fc}^{+/0}$ developed no observable photovoltages and showed no photocurrent at short circuit.

B. Spectral Response:

Spectral response data for electrodes sensitized with 8 dyes were also obtained, in order to characterize the grain boundary transport processes through the TiO_2 electrodes. The results can be explained fully by three coinciding factors. First, as expected, the spectral response roughly correlates with the absorption spectrum of each dye. Dyes which have lower extinction coefficients such as the RuL'_3 and OsL'_3 showed lower current responses. The wavelength at which the maximum photocurrent was observed corresponded to the

absorption maximum for each dye. Second, within a given set of ligands, the osmium dyes showed much more photocurrent at higher wavelengths. This phenomenon is due to the weak band present in the absorption spectra of the osmium dyes which is not present in the ruthenium dyes and which likely arises due to the population of triplet states in the osmium dyes. The only response which cannot be explained by a combination of these two effects is that of electrodes sensitized with the $\text{OsL}'_2(\text{SCN})_2$ dye. This dye shows very high light absorption, yet electrodes sensitized with this dye show very poor energy conversion. However, this effect can be explained by examining the ground state reduction potentials of the dyes. Of the dyes examined in this work, the $\text{OsL}'_2(\text{SCN})_2$ has the least positive reduction potential and in fact is only 0.18 V positive of the I_2/I^- redox couple. It is likely, therefore, that the smaller driving force for regeneration of the dye limits the efficiency of this dye.

C. Effect of pH on the TiO_2 Electrochemistry

$\text{TiO}_2/\text{RuL}'_2(\text{SCN})_2$ electrodes were characterized as a function of Proton Sponge concentration. In initial sets of experiments, each electrode was first characterized in a solution containing only buffered LiI/I_2 . When Proton Sponge was added, the open circuit voltages increased dramatically and the short circuit currents dropped. This effect is believed to be due to a shifting in the band edge position of the TiO_2 with pH. As the difference between the conduction band edge position of the TiO_2 and the reduction potential of the LiI/I_2 is increased, the open circuit voltage gets larger. If the conduction band edge becomes so negative that the excited dye cannot inject electrons efficiently, the short-circuit current density decreases. However, when the electrode was reintroduced to the buffered solution, the open-circuit voltages decreased as expected, but the short-circuit current densities did not recover.

As mentioned above, once the electrodes were exposed to iodine solution, the removal of the iodine contact caused some irreversible degradation of the electrode which could account for the change between the first and last potential scan. To determine whether

the decrease in current upon exposure to Proton Sponge was completely due to emptying the cell and refilling it, current-voltage curves of fresh $\text{TiO}_2/\text{RuL}'_2(\text{SCN})_2$ electrodes in solutions containing various concentrations of Proton Sponge were examined, The results for the 10 mM Proton Sponge solution were almost identical to those of electrodes first exposed to buffered solution. Since the dyes are known to desorb in aqueous base, the more basic solutions could cause some loss of dye even in non-aqueous solutions, resulting in lower currents when the electrodes are reimmersed in buffered solution. Although this effect may also account for part of the current decrease, the voltage increases in basic solution cannot be explained by a loss of dye, thus a band edge shift seems likely. The dark curves for this dye-electrode system show a similar shift in the voltage, further supporting the presence of a band edge shift. Table 2 summarizes the open circuit voltages and short circuit current densities as a function of Proton Sponge concentration.

D. Effect of pH on Luminescence of the Adsorbed Dye-- $\text{TiO}_2/\text{RuL}'_3$ Electrodes:

The effect of pH on the TiO_2 band edge positions was further examined through luminescence studies of the adsorbed dye. The quantum yield for luminescence (Φ) of the dye is given by eq. 1, where k_{rad} is the rate constant for radiative decay, k_{nrad} is the rate constant for non-radiative decay, and k_{inj} is the injection rate constant:

$$\Phi = \frac{k_{\text{rad}}}{k_{\text{rad}} + k_{\text{nrad}} + k_{\text{inj}}}$$

If a shift in the band edge position causes a decrease in the injection rate constant, resulting in a decrease in photocurrent increase, the quantum yield for luminescence should increase, and thus luminescence intensity should increase as the pH is increased. If the decrease in current observed above was solely due to a loss of dye, the luminescence intensity should decrease due to the smaller amount of dye on the surface of the electrode.

Luminescence studies were first attempted on $\text{TiO}_2/\text{RuL}'_2(\text{SCN})_2$ electrodes, but the luminescence intensity was very low and the peak was at a wavelength too positive to detect with the system available. $\text{TiO}_2/\text{RuL}'_3$ electrodes were chosen as an alternate because of the

strong luminescence of the L'_3 dyes. When Proton Sponge is present, the luminescence intensity increases, as expected. After 2 hours of immersion in the buffered solution after exposure to the Proton Sponge solution, the luminescence drops back down near the initial value. To minimize the effects of changing solutions, the luminescence experiment was repeated with a new electrode in a CH_3CN solution containing 0.001 M/0.001 M $\text{py}^{+/0}$. In this case, a few drops of glacial acetic acid were then added to the solution to neutralize the Proton Sponge. An immediate decrease in the luminescence intensity was observed, consistent with an increased dye injection efficiency and a positive conduction band edge shift due to the decreased pH.

To make sure the effect of pH on the current-voltage characteristics was not limited to the $\text{RuL}'_2(\text{SCN})_2$ system, J-E curves of the $\text{TiO}_2/\text{RuL}'_3$ electrodes were examined as a function of pH. The photocurrents dropped significantly when the Proton Sponge concentration was changed from 0 to 0.010 M. The large amount of hysteresis present makes it difficult to quantify the open-circuit voltage change although it appears to increase slightly. As in the previous case, the photocurrents decrease from their initial value on reimmersion and equilibration with the buffered solution. The dark curves show a large negative shift in the voltage when the electrode is exposed to Proton Sponge, similar to the behavior observed with the $\text{TiO}_2/\text{RuL}'_2(\text{SCN})_2$ electrodes. The dark curves return to their previous position when the electrode is reimmersed in the buffered solution.

E. Summary and Conclusions

The data collected in this project period appear to provide a rational approach for design of more efficient nanoporous electrodes. As discussed above, the first requirement for this type of system is slow charge transfer kinetics between the back contact of the electrode and the sacrificial electron donor/acceptor in solution. This condition allows the separation of charge by a diffusion gradient rather than drift. A similar approach has been used in single crystal systems such as Si, in which ohmic selective back contacts were used

in conjunction with Si electrodes with very high carrier lifetimes to produce efficient solar cells.

The effect of solution pH on the inter-facial energetics of the junction should be considered. The data demonstrate that changing the solution pH can have a profound effect on the current-voltage properties of the cell even in nonaqueous solutions. Increasing the pH has been shown to result in photovoltage increases of up to 200 mV. Again, though, this parameter needs to be optimized for the system studied. Studies of the effects of these properties on the electrochemistry of aqueous systems, and a comparison of the behavior of undoped and Nb-doped TiO₂ electrodes, are being performed at present.