

In view of the often-repeated (and generally true) statement about the easier reduction of polyhalides than monohalides (7), the original report of von Stackelberg and Stracke (2) that methylene chloride, CH_2Cl_2 , at the DME in dioxane-water is reduced at -2.33V whereas methyl chloride, CH_3Cl , with its single chlorine is easier to reduce, at -2.23V , is somewhat surprising. We have found that this unusual order of reduction is also true in anhydrous DMF at the DME.⁵ Considering the order of the half-wave potentials of CH_3Cl and CH_2Cl_2 at the DME, and the clearly discrete reduction of methylene chloride prior to methyl chloride that we have discovered at the carbon electrode, it seems highly possible that mercury is chemically involved before or during the potential-determining step at the DME in the electroreduction of methyl and methylene chlorides. This suggestion is in accord with a number of reports of chemical interaction of mercury with organic bromides (8).

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This is the fifth paper in the series "The Voltammetry of Organic Halogen Compounds;" parts IV and III were published previously (4, 9).

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⁵ The $E_{1/2}$ of CH_2Cl_2 is -2.17V and that of CH_3Cl , -2.10V (both vs. Hg pool) with a supporting electrolyte of 0.01M tetraethylammonium perchlorate in anhydrous DMF.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1975 JOURNAL. All discussions for the December 1975 Discussion Section should be submitted by Aug. 1, 1975.

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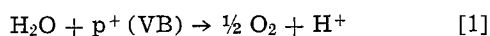
Semiconductor Electrodes

I. The Chemical Vapor Deposition and Application of Polycrystalline N-Type Titanium Dioxide Electrodes to the Photosensitized Electrolysis of Water

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A number of investigations on photoeffects on semiconductor electrodes have been reported (1, 2). Most studies have been concerned with single crystal semiconductor materials, although some polycrystalline semiconductors, e.g., SnO_2 (3-6), have also been used. Recently the photosensitized electrolytic oxidation of water on n-type TiO_2 single crystal electrodes has been described (7-9). In the absence of illumination the hole concentration in the valence band of n-type TiO_2 is very small, so that no appreciable anodic current flows for the oxidation of water, even at very positive potentials (9). When the electrode is irradiated with light with energy greater than the bandgap energy (ca. 3.2 eV), holes are formed in the valence band (VB) by excitation of electrons to the conduction band (CB). Under anodic polarization the bands in the semiconductor are bent in such a direction that the CB electrons migrate in the external circuit to the counterelectrode while the VB holes move to the surface where they combine with water molecules producing oxygen



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Unlike many other semiconductor materials (e.g., ZnO, GaAs), TiO_2 is stable with respect to dissolution under these conditions. These photoassisted electrolytic processes are obviously of interest with respect to the conversion of light to chemical and electrical energy. For practical applications, however, low cost polycrystalline electrode materials will probably be required for large area electrodes. Moreover, variation of the composition of the semiconductor (e.g., to change the bandgap or the donor or acceptor levels or to alter the surface states) leading to changes in spectral sensitivity or electrochemical behavior, can be accomplished more easily during the preparation of such polycrystalline materials. Mollers, Tolle, and Memming (10) have recently reported measurements of photocatalytic deposition on polycrystalline TiO_2 in 1M H_2SO_4 solutions. We report here details of the preparation of n-type TiO_2 electrodes by chemical vapor deposition (CVD) onto titanium metal substrates and a comparison of the photoassisted anodic oxidation of water on CVD and single crystal n-type TiO_2 .

The CVD technique employed was based on the method of Fitzgibbons, Sladek, and Hartwig (11), who studied dielectric thin films of TiO_2 for solid-state devices and integrated circuit applications. This technique involves the reaction of a titanium alkoxide and

water to produce TiO_2 and an alcohol. By utilizing vapors generated in a flask and delivered to the reaction site by a carrier gas, the reaction can be controlled in both rate and location. An alkoxide that produces a low boiling alcohol permits a low temperature of deposition; the only requirement is that the temperature is sufficient to boil off the resulting alcohol so that it will not be incorporated into the film. The reaction can be directed toward any suitable substrate simply by positioning the delivery tubes.

Experimental

The n-type TiO_2 on a Ti substrate was produced in the following manner (Fig. 1). Tetra-isopropyl orthotitanate from Eastman Organic Chemicals was heated in a flask in a water bath maintained at $80^\circ\text{--}85^\circ\text{C}$. Dry nitrogen (passed through CaCl_2 and molecular sieves) was used as a carrier gas; it was passed over the titanate and then through a delivery tube to the substrate. The tip of the delivery tube was located about 2.5 cm above the Ti substrate. Pure Ti was used as the substrate and was heated to about 150°C on a hot plate. The water vapor source also used nitrogen as the carrier gas. The water vapor was carried to the substrate through a tube parallel to the titanate delivery tube. Similar results could be obtained employing only water vapor from the air; however, an auxiliary water vapor source allowed shielding of the substrate from air currents which disrupt uniform film growth. To allow the development of a full space charge region in the semiconductor electrode, which can be as large as $10,000\text{\AA}$, depending upon carrier density, fairly thick TiO_2 films are required. Fitzgibbons *et al.* (11) reported that attempts to use continuous CVD to produce films thicker than $4000\text{--}5000\text{\AA}$ resulted in cracking of the films, but that heating the films between deposition allowed thicker films to be produced. The following CVD procedure was thus adopted.

The Ti substrate was cut into 1×1 cm squares, polished using very fine emery paper, and finally buffed to a mirror finish with a polishing wheel and rouge. This step was necessary to achieve good adherence of the TiO_2 and to promote growth of thicker layers. Unbuffered Ti (although polished with emery paper or etched in HF) gave films that were dull and nonuniform in appearance and which yielded much lower photocurrents. It was also difficult to achieve thicker films on unpolished material since flaking or formation of white powdered TiO_2 occurred when repeated depositions were attempted. A convenient film growth rate was established by adjusting the flow rates of the nitrogen over the titanium isopropoxide and water while watching the growth of interference rings on glass with white light. The polished Ti substrate was then placed under the nozzles and growth allowed for a given time period (typically about 2 min for the formation of two complete sets of interference rings). The substrate was then held in a bunsen burner flame for 3-4 min during which time the Ti turned red hot, the interference rings disappeared, and the surface took on a uniform, shiny, blue-gray appearance. After the flame treatment, the substrate was cooled in air briefly, then returned to the deposition apparatus for

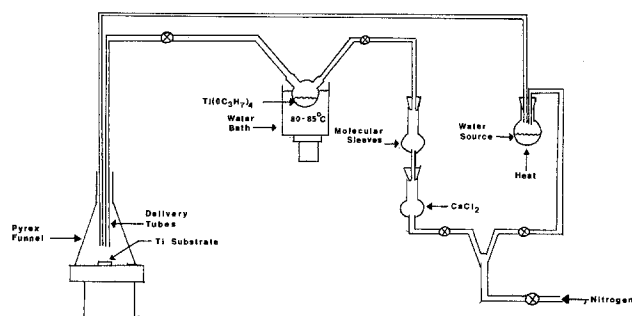


Fig. 1. Diagram of deposition apparatus

further CVD. Electrodes with between two and nine 2-min coatings were produced. The TiO_2 film thicknesses for these electrodes ranged from about 1.4 to 7μ , respectively.

The electrodes obtained by the above procedure showed a high resistance. They were placed in 10^{-5} Torr vacuum at 600°C for $1\frac{1}{2}$ hr. This treatment causes oxygen vacancies in the TiO_2 structure and produces n-type material with a much lower resistance. A copper wire was attached to the cleaned back of the Ti piece with silver epoxy cement (Epoxy Products Company), and the piece was mounted in a glass tube with silicone rubber cement (Dow Corning Corporation) so that only the surface covered by the TiO_2 was exposed to the solution.

The single crystal n-type TiO_2 was produced by National Lead Company and was given a similar vacuum-treatment. Ohmic contact was made with indium by ultrasonic welding, and it was mounted in glass using silicone rubber cement.

Some experiments were also attempted with TiO_2 produced anodically by oxidation of Ti substrates in 15% H_2SO_4 , 2% Na_3PO_4 , 5% Na_2HPO_4 , saturated H_3BO_3 , or 50:50 ethylene glycol saturated oxalic acid solutions (12). A 1×1 cm Ti piece was anodized for several hours in the electrolyte with greater than 10V applied. A metallic blue coating appeared immediately, but it changed little with time. These deposits are probably very thin, since production of the insulating TiO_2 film slows down or stops the anodization process.

All electrochemical measurements were performed with a multipurpose instrument constructed from solid-state operational amplifiers previously described (13-15). Current-potential curves were recorded with a Moseley Model 7005A X-Y Recorder. The electrode was illuminated through a quartz window in the cell wall. The counterelectrode was Pt and the reference electrode was a saturated calomel electrode (SCE).

Illumination was accomplished with a 200W mercury lamp (PEK-Illumination Industries). Either the full polychromatic output of the lamp was used, or the light was passed through a circular graded filter.

Results and Discussion

Current-potential curves for both single crystal and CVD TiO_2 (n-type) in the dark and under illumination in a 0.5M potassium chloride solution buffered at pH 6 are shown in Fig. 2. Curves at other pH's, from 1N NaOH to 1N H_2SO_4 are very similar to these on both the single crystal and CVD material, but are shifted in the negative direction 58 mV per unit increase in pH. The anodic region in the dark is characterized by a very low current until a certain breakdown potential when a marked current rise occurs. For the CVD TiO_2 this current rise occurs at potentials of about 2V vs. SCE and probably represents tunneling or film break-

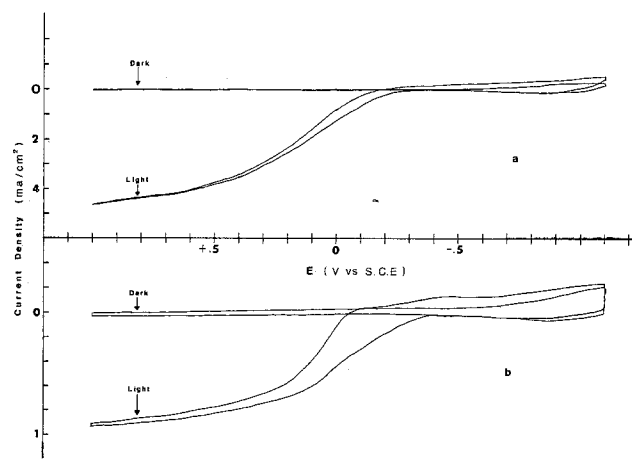


Fig. 2. Current density vs. potential for (a) single crystal TiO_2 , and (b) CVD TiO_2 in 0.5M KCl solution buffered to pH 6.

down; this region was not investigated further. A similar current rise, at somewhat less positive potentials, was noted by Möllers *et al.* (10). This effect appears similar to that observed when Ti is anodized, where the TiO_2 formation and passivation region is followed by breakdown. The single crystal TiO_2 shows no such current rise until potentials beyond 10V. On the reverse scan, or a cathodic scan from the open-circuit potential, in the dark, the potential rise occurs when hydrogen evolution commences, as evidenced by the appearance of gas bubbles on the electrode.

When the electrodes are illuminated with either polychromatic light or wavelengths corresponding to energies greater than the bandgap (e.g., 370 nm), anodic current and bubble formation on the electrodes is observed. The saturation oxidation current density under illumination is a function of light intensity and is somewhat smaller for the CVD TiO_2 than for the single crystal material. The higher C.D. observed with the single crystal material probably reflects the differences in structure between the CVD TiO_2 , which is a mixture of polycrystalline anatase and rutile (11), and the rutile single crystal. Thus, there may be better efficiency in light absorption, and hence generation of holes, as well as fewer hole-electron recombinations in the single crystal material. On the reverse scan into the negative potential region following oxidation under illumination a cathodic current larger than that observed in the dark is observed. This is attributed to the reduction of oxygen formed during the anodic scan, and is absent in scans into the cathodic region alone in the presence of light in deaerated solutions. In solutions containing dissolved air, a small cathodic wave is observed in this region on an initial cathodic scan. The wave observed on reversal from a photosensitized oxidation is about 4 times larger, suggesting that some of the oxygen produced anodically is adsorbed at the TiO_2 surface or that a saturated solution of oxygen is formed near the electrode surface.

The shift in the location of the photosensitized oxidation wave with pH is the same for both single crystal and CVD TiO_2 . A plot of E_L , the potential where the photocurrent commences *vs.* pH (Fig. 3), shows that both electrode materials fit the same linear correlation, with $\Delta E_L/\Delta \text{pH} = 58 \text{ mV/pH}$ unit. The spectral sensitivities of both materials, shown by photocurrent *vs.* wavelength plots (Fig. 4), are also virtually identical.

The CVD TiO_2 is very stable at open circuit, to solutions ranging in pH from 0 to 14 (1N H_2SO_4 to 1N NaOH), as is the single crystal material; no noticeable decreases in saturation current densities occurred with prolonged immersion. The CVD TiO_2 is also mechanically stable, and withstands gentle polishing with very fine emery paper, although scraping the surface will destroy the film. Prolonged exposure of the CVD TiO_2 to positive potentials, with and without light, showed no noticeable changes in the appearance of the coating or maximum current density. Prolonged cathodic evolution of hydrogen occasionally produced small

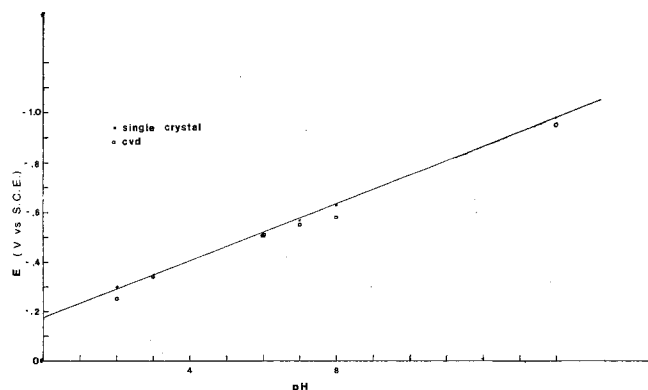


Fig. 3. E_L vs. pH for single crystal and CVD TiO_2

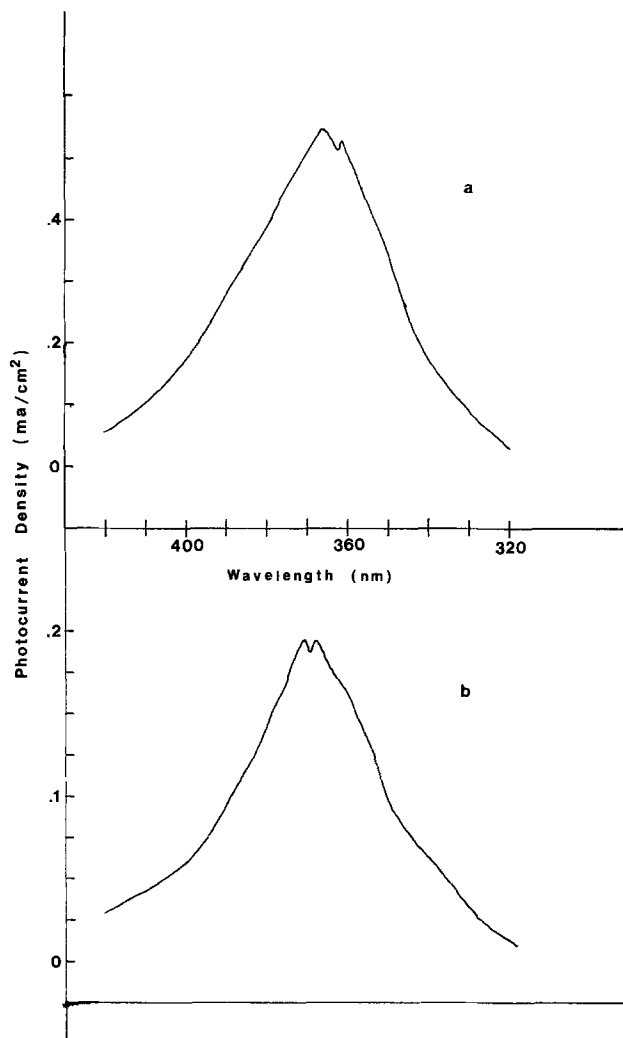


Fig. 4. Photocurrent vs. wavelength at potential of $+0.775\text{V}$ (vs. SCE) for (a) single crystal TiO_2 , and (b) CVD TiO_2 . Curves are uncorrected for mercury lamp emission and transmittance variations of circular graded filter.

blisters or flakes on scattered portions of the surface. This may indicate poor adhesion of the TiO_2 film to the Ti substrate in these areas, perhaps because of some contaminant on the substrate prior to deposition.

A brief study of the photosensitized oxidation of water on a TiO_2 film produced by anodization of Ti was undertaken to compare its behavior to that of the CVD material. Small photocurrents were observed on the anodized Ti, but the current densities were about 30-40 times lower than that of CVD TiO_2 . The shift in potential of the anodized Ti at open circuit upon exposure to light (ca. -0.10V in 1M KCl) was also smaller than that observed for CVD or single crystal TiO_2 (ca. -0.50V in 1M KCl). This behavior suggests that the TiO_2 film formed on anodization of Ti is of insufficient thickness to support a full space charge, and it may also differ structurally from that of CVD TiO_2 .

The CVD deposition technique can also be used to deposit TiO_2 upon glass [see also Ref. (10)], suggesting possible applications as a transparent electrode material, particularly in the region of negative potentials where SnO_2 electrodes sometimes are not useful. Moreover, the good stability of these CVD TiO_2 electrodes may make them useful in other electrolytic processes, for example, for photoassisted oxidations or reductions of organic materials in nonaqueous solvents. These applications are currently under investigation.

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DISCUSSION SECTION



This Discussion Section includes discussion of papers appearing in the *Journal of The Electrochemical Society*, Vol. 121, No. 8 and 12; August and December 1974.

The Electroreduction of Oxygen and Hydrogen Peroxide on Sodium-Tungsten Bronzes

J.-P. Randin (pp. 1029-1033, Vol. 121, No. 8)

J. McHardy:¹ The paper under discussion largely bears out the findings of earlier workers² but two observations do call for comment. The first is that the presence of platinum in a bronze crystal did not increase its electrocatalytic activity for oxygen reduction and the second is that the $\log i$ vs. E curve for hydrogen peroxide reduction passed through a maximum.

In the 8 years since Sepa *et al.*³ first reported sodium tungsten bronze to be an electrocatalyst for oxygen reduction, many publications have appeared on this and related subjects.² Several workers⁴⁻⁷ were able to reproduce Sepa's results, but only by incorporating platinum in the bronze crystals. Other papers also reported beneficial effects of platinum upon electrocatalysis although Randin cites two of them^{8,9} as evidence that platinum had no effect. Detection of the electrocatalysis is not a simple matter because the limiting current density for oxygen reduction is quite low (10-100 times lower than the diffusion controlled current observed at large overpotentials) and can easily be masked, *e.g.*, by corrosion currents.

Comparison of Randin's data with those of workers who did reproduce Sepa's results reveals differences both in condition and technique. Most significantly, Randin used more concentrated acid (tending to ag-

gravate corrosion problems) and limited his measurements to relatively high current densities ($\geq 10^{-5}$ A/cm²). In my own work,⁷ platinum-induced electrocatalytic activity was observed only after reducing corrosion currents to 10^{-6} A/cm² or less and even then it was confined to current densities below 10^{-5} A/cm².

Turning to the second point, I would draw attention to the work of Voinov and Tannenberger¹⁰ who also examined the reduction of hydrogen peroxide on tungsten bronzes. Despite differences in the interstitial element (they used Ce_xWO_3 and Yb_xWO_3) kinetic data at the rotating electrode were quite similar. Unlike Randin, however, Voinov and Tannenberger reported no maximum in the $\log i$ - E curve. The disagreement casts some doubt on Randin's interpretation of the maximum and raises the possibility that it may have been an experimental artifact.

J.-P. Randin:¹¹ Among the various published investigations in which oxygen reduction reaction on sodium-tungsten bronzes was studied, only McHardy's work⁷ and the paper under discussion include a detailed quantitative evaluation of the effect of platinum incorporated by using a platinum anode (or crucible) during the preparation of the bronzes by electrolysis of a polytungstate melt. Other workers also reported various effects of platinum incorporated by extended potential cycling in acid solutions containing Pt metal ions⁸ or by electrodeposition from chloroplatinic acid.¹² The latter methods gave relatively high surface concentrations of Pt as compared to the low bulk concentrations (in the ppm range) involved in the study under discussion. These studies^{8,12} are therefore not relevant to the specific criticisms of McHardy.

It is evident from both McHardy's work¹³ and from our own¹⁴ that a significant corrosion current is ex-

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² For a review of the relevant literature through 1973 see J. McHardy and P. Stonehart, in "M.T.P. International Review of Science, Physical Chemistry," Series 2, Butterworths, London (In Press).

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