Semiconductor Electrodes. II. Electrochemistry at n-Type TiO_2 Electrodes in Acetonitrile Solutions

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Abstract: The electrode response of single crystal n-type TiO_2 in acetonitrile was investigated with a large number of electroactive compounds differing widely in their standard potentials. The electrochemical behavior of various compounds can be used to investigate the band structure of the semiconductor electrode. This method is useful in detecting intermediate energy levels between the conduction and valance bands capable of mediating electron transfer and in assigning energies to these levels. For TiO_2 at least one intermediate energy level was located about 1.2 eV below the conduction band. Polycrystalline TiO_2 was shown to respond in a similar fashion indicating that the intermediate energy level is characteristic of n-type TiO_2. A comparison of the behavior of metal and semiconductor electrodes as a function of the redox potential of various couples and the effect of light on oxidations at the TiO_2 electrode is discussed.

Semiconductors show promise as electrodes for electrochemical processes.[1] In part this is because of the energy specificity of semiconductor (SC) reactions. A change in the potential of a SC electrode often results in large changes in the number of charge carriers (electrons or holes) at the SC-electrolyte interface but in very little modulation of the energies of the valence and conduction bands at the SC surface through which electron transfer must occur (in the absence of such complicating factors as surface states or energy levels between the conduction and valence bands). Only those solution redox couples with energies near the conduction or valence bands can exchange electrons with the electrode[1] so that SC electrodes may be used to probe the mechanism of electrode reactions.[2] Moreover changes in mechanism leading to different products than those obtained at metal electrodes may be possible (e.g., a reaction which is ECE at a metal electrode may be EC at a SC) with attendant synthetic implications.[3] Recently, the possible exploitation of photoeffects at SC electrodes for solar energy conversion and storage has been discussed[4] and an electrochemical cell utilizing a n-type TiO_2 electrode for carrying out the photodecomposition of water to O_2 and H_2 was recently demonstrated.[5] Similar photo effects may also have synthetic implications in organic electrosynthesis perhaps by using sunlight as an energy source to drive the desired electrode reactions. A knowledge of electrode behavior in nonaqueous solvents would be especially useful in this area since water is often not a satisfactory solvent for organic synthesis. By exciting solution species with light instead of the electrode, it may also be possible to study the electrochemistry of excited states with SC electrodes,[1,5] because quenching of excited states by the electrode should be of less importance for SC compared with metal electrodes.

To date nearly all experimental studies have been concerned with semiconductor-aqueous solution interface. However, aqueous media are often not suited for studies probing the electrochemical properties of semiconductor electrodes. Adsorption of impurities, even from rigorously purified aqueous systems, can contaminate the electrode surface. Under these circumstances, reproducible background and faradaic currents at solid electrodes may be difficult to obtain. The adsorbed impurities may also generate surface states, confusing the issue of solution and SC related phenomena.[1] Water also has a rather limited thermodynamic (1.23 V) and practical (ca. 1.5 V) stability range for electrochemical studies. This severely limits the potential range of stable redox couples available for study and increases the probability of undesirable electron transfer reactions between the solvent and electrode. Finally, there are a relatively small number of simple and reversible redox couples involving soluble reactants and products within the stability range of water.

Many of these problems can be eliminated or at least minimized by using a nonaqueous solvent. Adsorption of impurities is known to occur to a lesser extent in nonaqueous solvents. Dissolution of the electrode into its ionic components at positive potentials and during illumination, often an undesirable reaction in aqueous solutions, should be less of a problem since solvation of the ions composing the SC lattice, which is a major factor in the dissolution, is usually not as strong as in water. Many aprotic solvents have a larger difference between the energies of solvent oxidation and reduction than does water (e.g., ca. 5 V for acetonitrile). Moreover, a large number of reversible redox couples with a wide range of standard potentials are available in a number of nonaqueous solvents.

With these considerations in mind, we have undertaken the investigation of the electrochemical behavior of n-type TiO_2, a wide band gap SC (E_g = 3 eV) in acetonitrile (ACN). Our aim in the present investigation was to probe the relation between band structure and reactivity of solution species and, if possible, map the band gap region to determine the presence and energies of any intermediate bands or surface states. We have chosen to do this by studying the electrochemical behavior of a large number of compounds comprising a broad range of formal redox potentials and hence a broad energy range. In a previous investigation by Gomes and Cardon,[6] a single redox couple, $Fe(CN)_6^{4-}$-$Fe(CN)_6^{3-}$, was used to probe the band structures of a number of different SC materials.[6] The use of a single couple, however, can probe only a narrow energy range. Where more than one redox couple was used, the energy distribution of the couples was such that all could exchange electrons with the conduction band and the possible participation of surface states was not taken into account.[7] We were also interested in studying the effect of light on SC electrode processes of organic species in ACN.

Experimental Section

Most of the compounds used in this study were obtained from commercial sources and in many cases purified by three to five recrystallizations from the appropriate solvent or solvents. $Ru(TPTZ)_2(ClO_4)_3$ (TPTZ = 2,4,6-tripyridyl-*s*-triazene) and $Ru(bipy)_3(ClO_4)_2$ (bipy = bipyridine) were prepared as described in the literature.[8] All of these compounds have been previously characterized in this laboratory and shown to be of satisfactory purity. However, to ensure that no decomposition or contamination

Table I.[a] Peak Potentials for Reductions and Reoxidations of Compound Used in This Study

	Pt	TiO$_2$	
	$E°$ (V vs. SCE)	E_{pc}	E_{pa} (V vs. SCE)
Ru(bipy)$_3{}^{3+}$	+1.3	+0.36	None
	−1.3	−1.34	−1.27
	−1.49	−1.52	−1.46
	−1.73	−1.77	−1.70
Th·$^+$	+1.23	+0.4	None
10-MP·$^+$	+0.82	+0.28	None
TMPD·$^+$	+0.22	−0.31	None
Ox-1·$^+$	−0.42	−0.8	None
	−1.3	−1.65	None (adsorption prob)
p-BQ	−0.52	−1.0	None
	−1.64 (irreversible)	−1.89	None
Ru(TPTZ)$_2{}^{3+}$	−0.81	−0.9	−0.72
	−0.97	−1.09	−0.88
	−1.63	−1.76	−1.55
	−1.88	−2.03	−1.83
AQ	−0.94	−1.12	Some ox. beginning at ca. −0.9
	Ca. −1.61 (quasireversible)	−1.84	−1.44
DBM	−1.55	−1.68	−1.44
9,10-DPA	−1.84	−1.93	−1.74
A	−1.94	−2.06	−1.80

[a] Abbreviations used in this table: Th, thianthrene; 10-MP, 10-methylphenothiozine; TMPD, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine; Ox-1, oxazine-1; *p*-BQ, *p*-benzoquinone; AQ, anthraquinone; DBM, dibenzoylmethane; 9,10-DPA, 9,10-diphenylanthracene; A, anthracene.

had occurred, their electrochemical behavior was investigated at a platinum electrode in the same cell and solvent as that used for the TiO$_2$ study. For some experiments, certain of the compounds (Ru(bip)$_3{}^{2+}$, thianthrene) were converted to a more convenient oxidation state by controlled potential electrolysis at a platinum gauze electrode prior to the experiment and either used immediately or precipitated as the perchlorate salt for later use.

Polarographic grade tetrabutylammonium perchlorate (TBAP), the supporting electrolyte in all experiments, and acetonitrile were dried and purified as described previously.[9]

The TiO$_2$ single crystal used for fabrication of the electrode was cut from a larger crystal obtained from National Lead. The crystal was about 1 mm thick, cut perpendicular to the C$_2$ axis; this face was exposed to the solution. The crystal was heated at 650° for 1 hr in vacuum before mounting. Ohmic contracts were made with indium solder. The surface to be exposed was polished smooth with 0.5μ alumina polishing powder. The electrode was mounted on a flat piece of glass which was itself connected to a glass tube with silicone rubber adhesive (Dow-Corning and General Electric). The silicone rubbers were shown not to swell or to leach in detectable quantities electroactive or adsorbable impurities. The rubbers were not attacked by most acids or bases although eventual degradation was observed after repeated or prolonged exposure to HF. The electrical connections to the electrode ran through the glass tube. The electrode was masked to an area of about 0.5 cm^2 by cementing a piece of frosted glass containing a circular hole to the front surface of the semiconductor. Care was taken to ensure that no solution could seep between the glass pieces and the semiconductor. The edges of the semiconductor were coated with the silicone adhesive. The polycrystalline TiO$_2$ electrode was prepared by chemical vapor deposition of TiO$_2$ on a Ti-substrate, as previously described.[10]

Before each experiment, the TiO$_2$ electrode was exposed to an HF etching solution for 10 sec and then dipped into concentrated HNO$_3$ for several seconds. The electrode was rinsed with distilled water and dried in vacuum for 1 hr. The composition of the etching solution was the same as that used by Honda and Fujishima.[4]

The cell used in these experiments was of a three-compartment design with the auxiliary and reference compartments being removable glass tubes slanted toward the working electrode. The distance between the tips of the tubes and the working electrode was about 1 cm. The ends of the glass tubes were closed with medium porosity fritted-glass disks to prevent mixing of the solutions in the various compartments. The main compartment containing the working electrode had an optically flat Pyrex window. All joints were of ground glass.

The platinum working electrode used in conjunction with the semiconductor electrode was a small disk (about 0.75 mm^2) sealed in glass and was polished before each use with 0.5μ alumina polishing powder. The auxiliary electrode was a platinum wire and the reference electrode, a silver wire. The potential of this reference electrode was determined during each experiment by obtaining the cyclic voltammogram of the redox couple being used to probe the semiconductor at the platinum electrode. In most cases, these redox couples had a known formal potential in ACN with respect to an aqueous saturated calomel electrode (SCE) under similar experimental conditions. In a few cases, the solvent was DMF. This introduces only a small change in the potentials reported for these couples from that in ACN. All potentials are reported vs. the aqueous SCE.

Most experiments were carried out under an inert helium atmosphere in a Vacuum/Atmospheres Corporation (Hawthorne, Calif.) drybox. When it was necessary to work outside the box, the cell was sealed with silicone vacuum grease. A Teflon thermometer adapter was used to adapt the semiconductor electrode for use with the cell.

A PAR Model 173 potentiostat and a PAR Model 175 universal programmer (Princeton Applied Research Corp., Princeton, N.J.) were used for electrochemical experiments. Current voltage curves were recorded on a Houston Instruments Model 2000 *x-y* recorder. Capacitance measurements were made with the aid of a PAR lock-in amplifier Model HR-8. Photoexcitation experiments were carried out using a 200-W mercury lamp and circular graded filter.

Results

Cyclic voltammograms at TiO$_2$ of blank electrolyte solutions showed no faradaic processes for positive potentials up to +7 V when the scan was begun at 0 V. Only a very small capacitive current (ca. 1 μA) was seen. When the direction of the scan was toward negative potentials, a reductive current (ca. 5 μA) was observed beginning at about −0.8 V. The current increased in an irregular manner until the reduction of the tetrabutylammonium ion commenced at about −2.8 V. In most experiments, this current was only a small fraction (i.e., less than 10%) of the currents observed for the reductions of the added electroactive compounds. The origin of this current is not known but may correspond to the reduction of residual water.

In experiments where compounds were added to probe the behavior of the TiO$_2$ electrode, voltammograms were obtained at both a platinum disk working electrode and at the TiO$_2$ electrode. In all cases, cyclic voltammetric studies showed that the compounds were reversibly reduced and ox-

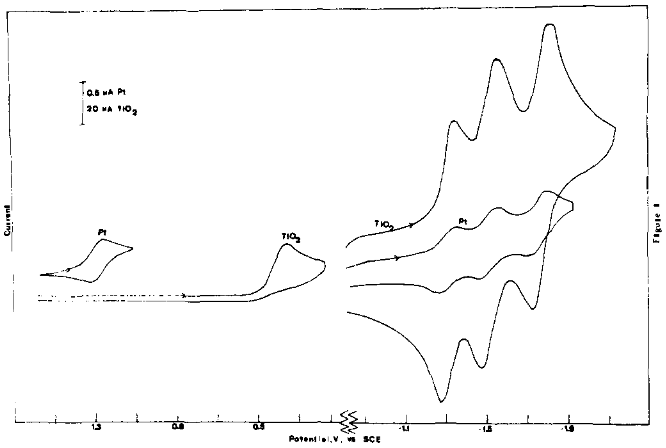

Figure 1. Cyclic voltammogram of a 0.4 m*M* solution of $Ru(bipy)_3^{3+}$ at single crystal TiO_2 and Pt electrodes. Potential sweep rate was 0.2 V/sec.

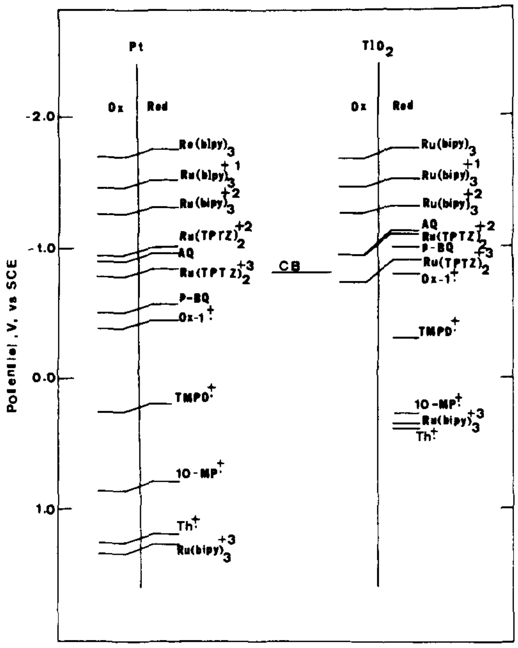

Figure 2. The reduction and reoxidation peak potentials of some of the compounds used in this investigation. Potentials were obtained at a sweep rate of 0.2 V/sec.

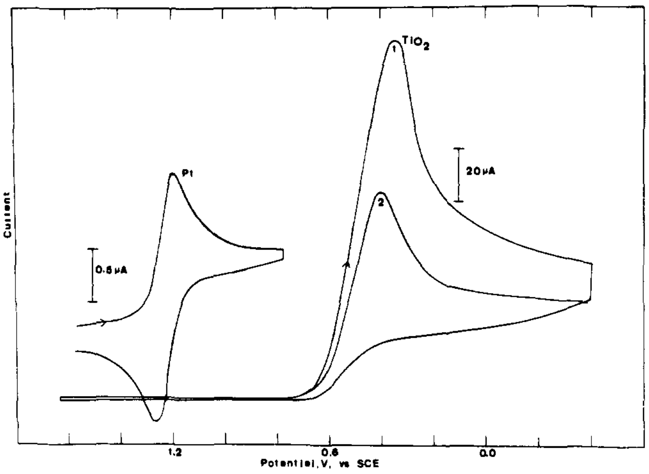

Figure 3. Cyclic voltammogram of thianthrene radical cation, $Th^{\cdot+}$: (1) first potential sweep cycle: (2) second potential sweep cycle. The $Th^{\cdot+}$ concentration was 1.2 m*M*. The sweep rate was 0.2 V/sec. The behavior at both TiO_2 and Pt is shown.

idized at the platinum electrode (except for the second reduction of *p*-benzoquinone which is irreversible and of anthraquinone which is quasireversible). The cyclic voltammograms at platinum served both to calibrate the reference electrode and to give an immediate indication of the differences in behavior between platinum and TiO_2. Compounds were chosen on the basis of the potentials at which their reductions occur since an n-type semiconductor is not expected to be as effective for oxidations as it is for reductions.[1] Some of the compounds underwent consecutive reductions at progressively more negative potentials at platinum, and this permitted several potential regions to be investigated at TiO_2 with one compound. $Ru(bipy)_3^{3+}$, for example, is reduced in four steps covering a potential range of about 3 V (Figure 1).[8]

The peak potentials for the reductions and reoxidations of a representative number of the compounds in this study under voltammetric conditions are given in Table I and Figure 2 for both platinum and TiO_2. That the wave peaks correspond to diffusion-limited processes at TiO_2 is shown in Figure 3 for the reduction of thianthrene radical cation. The decrease in peak height on the second sweep reflects the depletion of compound near the electrode during the first potential scan.

The peak potentials and wave shapes at TiO_2 were often a function of sweep rate and compound concentration. This probably reflects both the less reversible nature of the electron transfer at TiO_2 for certain of the compounds and the uncompensated portion of the TiO_2 electrode resistance. Positive feedback resistance compensation was used for all experiments but, as has been previously noted, compensating for the internal resistance of the electrode (about 2000 Ω) was difficult.[11] To minimize internal resistance drop difficulties, compound concentrations were generally less than 1 m*M*. By judicious adjustment of the internal resistance compensation (to a point just short of potentiostat oscillation), it was possible to obtain reversible behavior for the three most negative reductions and oxidations of $Ru(bipy)_3^{3+}$ (Figure 1). The estimated maximum uncertainty of the potentials in Figure 2 is 100 mV.

For *p*-benzoquinone and oxazine-1 cation, successive potential sweeps of the first reduction wave resulted in a negative shift of the wave of 40 to 80 mV and some change in wave shape. When the sweep was continued beyond the second reduction wave, faradaic currents decreased to zero at the foot of the second wave on sweep reversal. These phenomena appear to be adsorption related.

Three potential regions are immediately evident in Figure 2. In the area which is positive of about −0.8 V, couples that are reversible at platinum are totally irreversible at TiO_2 with only reductions possible. In some cases, the reduction wave is shifted by as much as 1 V to more negative potentials compared with platinum (Figures 1 and 3). Couples reduced and oxidized between about −0.8 and −1.0 V may either be nearly reversible, e.g., $Ru(TPTZ)_2^{3+}$ (whose behavior on TiO_2 is very nearly the same as on Pt), or nearly irreversible, e.g., anthraquinone (Figure 4), at TiO_2. There is some reoxidation evident for anthraquinone in Figure 4, but the rate is nearly potential independent and far from diffusion limited. This potential region appears to be a transition region between reversible and irreversible electrochemical behavior. Compounds reduced negative of −1.0 V are reversible at both platinum and TiO_2 (Figure 1) within the limits of the uncertainty of potential at TiO_2. The exceptions are the second reductions of anthraquinone and *p*-benzoquinone which are not reversible at platinum and the

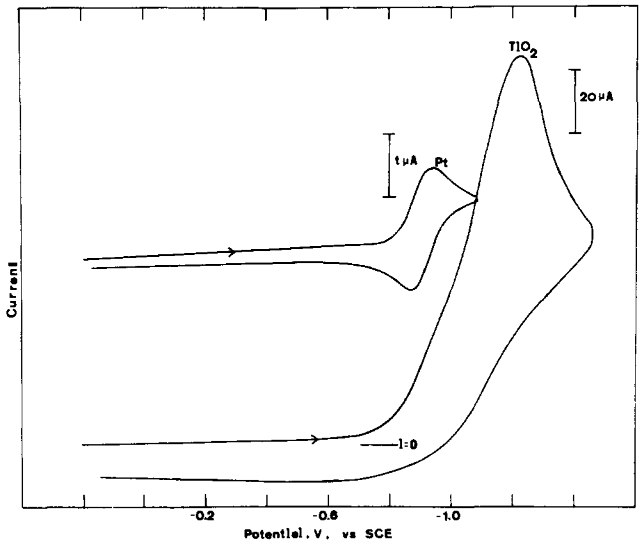

Figure 4. Cyclic voltammogram of anthraquinone at TiO_2 and Pt. The concentration was 0.75 m*M* and the sweep rate 0.2 V/sec.

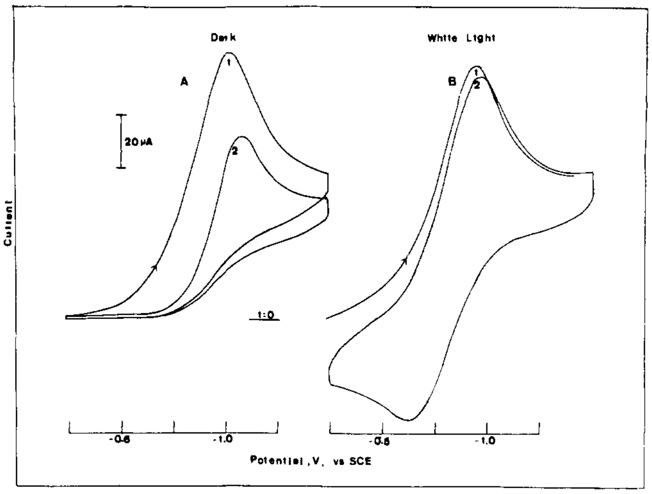

Figure 5. Cyclic voltammogram at 0.2 V/sec of *p*-benzoquinone at TiO_2. The concentration was 0.8 m*M*: (A) dark; (B) in presence of white light from a 200-W mercury lamp.

oxazine-1 cation which is complicated by the probable adsorption problems.

Closer inspection of Figure 2 shows that the compounds reduced positive of +0.4 V at platinum are all reduced at between +0.3 and +0.4 V at TiO_2 even though their redox potentials differ by as much as 0.5 V. The reductions for the compounds reduced at platinum between +0.4 and −1.0 V begin at nearly the same potential as at platinum though their wave peaks are shifted by as much as 0.5 V.

Oxidations often do not occur at n-type semiconductors either because the reduced species is energetically located in the band gap or, if energetically near the valence band, because the number of holes in the valence band is not sufficient to sustain a measurable reaction rate.[1] However, oxidations can occur both for compounds in the gap region and near the valence band when light of the same energy as the band gap illuminates the electrode. These reactions occur because vacancies or holes are created near the electrode surface. To see if oxidations were possible when the TiO_2 electrode was illuminated for some of the irreversibly reduced compounds, a number of photosensitization experiments were undertaken. Figure 5a shows the cyclic voltammogram for *p*-benzoquinone in the dark. The reduction is irreversible, and the decrease in peak height on successive sweeps shows that the solution near the electrode is being depleted of compound. Figure 5b shows what happens when the electrode is illuminated with white light from a 200-W mercury lamp. Although the *p*-benzoquinone system is not Nernstian (i.e., showing a 58-mV peak separation), it is reoxidized on scan reversal and shows only a small decrease in the reduction peak height on successive scans. The height of the oxidation wave is a function of the light intensity decreasing as the intensity decreases. The height of the reduction wave on the first scan is decreased somewhat during illumination. Moreover, the oxidation wave occurs at potentials negative of its location at platinum. Illuminating with light of energy less than that of the band gap did not promote measurable oxidation.

We were unable to demonstrate similar phenomena for the compounds reduced positive of +0.4 V. Oxidation of solvent occurs quite readily at these potentials during illumination obscuring any reoxidations. For example, an attempted oxidation of thianthrene under illumination with the TiO_2 electrode scanned toward positive potentials failed to show any reduction of the thianthrene cation radical on sweep reversal.

By superimposing a small AC signal on the applied DC potential for pure electrolyte solutions, the capacitance and resistance of the TiO_2 electrode may be determined by measuring the various phase relationships of current and potential.[1] The resistance of the TiO_2 electrode determined by this method was about 2 kΩ. A plot of $1/C_{sc}^2$ against potential according to the Schottky-Mott equation (eq 1)

$$1/C_{sc}^2 = 2/\epsilon\epsilon_0 e_0 C_D(\Delta\phi_s - kT/e_0) \qquad (1)$$

yields information about the donor density (from the slope) and flatband potential (from the intercept), where C_{sc} is the capacitance of the TiO_2 electrode (essentially the same as the total measured capacitance of the semiconductor–electrolyte interface), ϵ and ϵ_0 are the dielectric constant of the semiconductor and permittivity of free space, respectively, e_0 is the absolute value of the electronic charge, C_D is the donor density, k is the Boltzmann constant, and $\Delta\phi_s$, the potential difference between the flatband potential and the potential at which the measurement is made. The results of these measurements for three different frequencies are shown in Figure 6. The donor concentration determined from these plots, assuming ϵ for TiO_2 is 100, is about 10^{16} cm^{-3}. The measured flatband potential was -1.5 ± 0.20 V. The apparent dependence of the flatband potential on frequency is discussed below.

The electrochemical properties of the polycrystalline TiO_2 electrode were very similar to those of the single crystal electrode. However, its internal resistance was lower, and little trouble was encountered in obtaining reversible electrochemical behavior for couples with standard potentials negative of −1.0 V. The reduction potentials for the irreversibly reduced compounds differed by no more and usually by much less than 100 mV in going from the single crystal to the polycrystalline electrode. In all cases, any discrepancy could be attributed to the higher resistance of the single crystal electrode. The properties of polycrystalline TiO_2 under photoexcitation have been reported previously.[10,12] The effect of light is the same for the single crystal and polycrystalline materials, although the magnitude of the effect is less for polycrystalline TiO_2.

Discussion

The rectifying properties of semiconductor–electrolyte interfaces are well known.[1] For an n-type semiconductor like TiO_2, this means that oxidations usually do not occur unless the electron level distribution of the reduced species

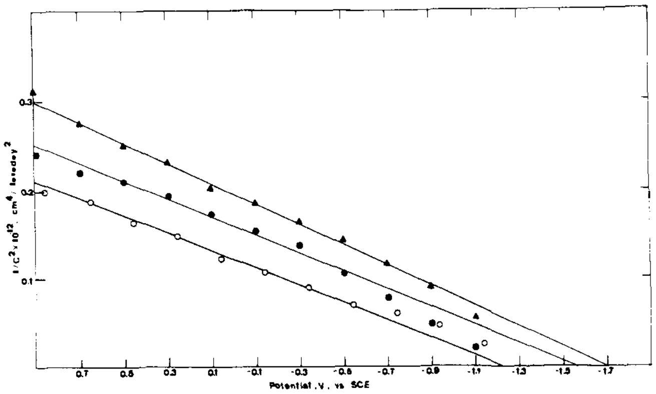

Figure 6. Schottky–Mott plots of capacitance vs. electrode potential for TiO_2 in acetonitrile: (▲) 200 Hz; (●) 500 Hz; (○) 1000 Hz.

is energetically near or above the conduction band. However, the rate of an oxidation in the conduction band region is usually potential independent. It would not be possible to observe reversible cyclic voltammetric behavior at TiO_2 if the rate of the oxidation was potential independent. Since the oxidation of compounds with redox potentials negative of -1 V (Figure 2) occurs with cyclic voltammetric reversibility, variation of the potential difference between SC and solution not only modulates the carrier concentrations near the surface but also causes changes in the surface potential of the semiconductor with respect to the bulk solution. Such modulation of the surface potential can occur when the number of charge carriers at the semiconductor surface approaches the density of states at the bottom of the conduction band.[1] When this occurs, degeneracy begins and the electrode behavior becomes metal-like. The density of states in most semiconductors is about 10^{19} cm^{-3}.[6] For a semiconductor with a donor density of 10^{16} to 10^{17} cm^{-3}, degeneracy begins at 100–200 mV negative of the flat band potential. Since $Ru(TPTZ)_2{}^{3+}$ is reversibly reduced or nearly so at about -0.8 V, the flat band potential (V_{fb}) must lie somewhat positive of this by 100–200 mV. The energy or its potential equivalent vs. an SCE of the conduction band can be determined from the flat band potential (V_{fb}) from the relation[6]

$$-E_c(\text{eV}) = e_0V_{fb} + kT \ln (C_D/N_c) = e_0V_c \qquad (2)$$

where N_c is the density of states at the bottom of the conduction band. For the TiO_2 electrode used in this work V_c is about -0.8 V. This is the potential of an electron at the bottom of the conduction band vs. its potential in the SCE reference electrode. Its energy, E_c, is 0.8 eV vs. an SCE. Capacity measurements predict a V_c negative of this value; this discrepancy is discussed below. The energy of the conduction band at the surface does not change with applied potential for potentials positive of V_{fb}.

Redox couples with standard potentials near V_c may or may not be reversibly reduced and oxidized. The deciding factor is the energy level distributions of the oxidized and reduced species in solution, $W_{ox}(E)$ and $W_{red}(E)$,[13] where $W_{red}(E)$ is given by

$$W_{red}(E) \propto \exp[-(E - E°_{redox} + \lambda)^2/4kT\lambda] \qquad (3)$$

and $W_{ox}(E)$ is defined similarly; $E°_{redox}$ is the energy corresponding to the standard potential, $V°_{redox}$, of the redox couple, and λ is the energy difference between $E°_{redox}$ and the maximum value of $W_{red}(E)$ or $W_{ox}(E)$.[13] In physical terms, λ represents the reorganizational energy between the oxidized and reduced forms on electron transfer and can be approximated by methods described by Marcus.[14] The intersection of the distributions $W_{red}(E)$ and $W_{ox}(E)$ occurs at $E°_{redox}$ (see Figure 7).

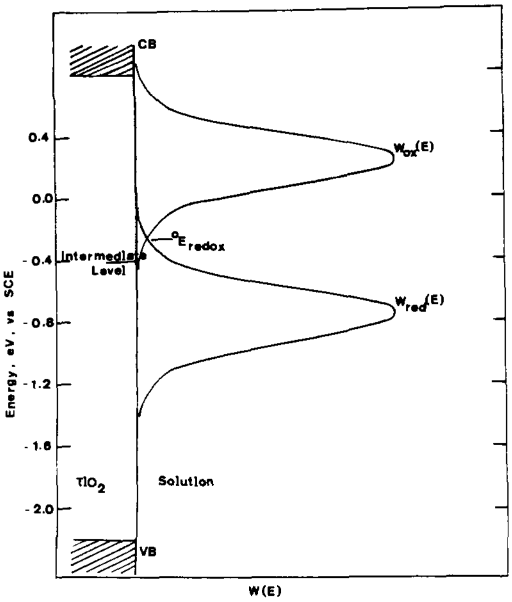

Figure 7. Relationship between the TiO_2 band structure and the solution energy distribution for the redox couple TMPD-TMPD·$^+$ assuming a λ of 0.5 eV.

Electron transfer cannot occur if $W_{red}(E)$ (or $W_{ox}(E)$) does not have a significant value at E_c since electron transfer must be isoenergetic.[1] For small λ values, when $E°_{redox}$ is near E_c, $W_{red}(E)$ will have significant values at energies above E_c. When degeneracy occurs and V_c moves negative (E_c increases), an oxidation will continue to occur and its rate will be potential dependent. On the other hand, if λ is large and $E°_{redox}$ is near E_c, the value of $W_{red}(E)$ at E_c will be small and an oxidation will soon cease when the surface becomes degenerate. In both cases, the rate of an oxidation will become independent of potential for potentials positive of V_{fb}. Couples with redox potentials near V_c can display either behavior depending upon the magnitude of λ. $Ru(TPTZ)_2{}^{3+}$ and anthraquinone may typify this behavior.

For compounds with standard potentials significantly positive of V_{fb}, the rate constant for a reduction, k, can be represented by (4)[1]

$$k = k_r(E)W_{ox}(E_c)n_s \qquad (4)$$

where n_s, the density of electrons at the semiconductor surface in the conduction band, is proportional to $\exp(\Delta\phi_s/kT)$. A reoxidation of the reduced compound will not occur because $W_{red}(E_c)$ is too small for a measurable rate (Figure 7). When the electrode potential is equal to or negative of $V°_{redox}$, reduction is thermodynamically possible but may be slow because of the small value of n_s. As the potential is made more negative, the rate will increase until eventually it becomes diffusion controlled; p-benzoquinone, oxazine-1 cation, and TMPD·$^+$ show this behavior. Very rapid rates of reduction are not expected until the potential of the flat band, V_{fb}, is reached, because of the depletion layer at the electrode surface. Diffusion-limited rates are not observed for p-benzoquinone and oxazine-1 cation except at potentials negative of V_{fb}. The difference in their peak potentials may be satisfactorily explained by relatively small differences in their λ values. TMPD·$^+$ on the other hand is reduced at diffusion-controlled rates at potentials considerably positive of V_{fb}, despite the very few charge carriers in the conduction band at the surface. Surface states or an intermediate band may be implicated in this reduction of TMPD·$^+$ (see Figure 7).

It is unlikely that thianthrene cation radical, Ru(bipy)$_3^{3+}$, and 10-MP$\cdot^+$ are reduced via the conduction band. The λ values in acetonitrile for aromatic compounds are usually not much greater than 1 eV.[15] This places the maximum of $W_{ox}(E)$ for thianthrene and Ru(bipy)$_3^{3+}$ at −0.2 eV (vs. 0.8 eV for the conduction band) and, at E_c, $W_{ox}(E_c)$ is only about 10^{-4} of its maximum value. In addition we calculate n_s to be infinitesimal at the potential where the rates for the reduction of these compounds first become diffusion controlled (+0.4 to +0.3 V). The very small values of these two factors makes reduction via the conduction band improbable.

Tunneling directly into the conduction band in the interior might be invoked to explain these results but this is unlikely at the doping levels of the TiO_2 electrode in these experiments.[16] Instead, we feel that the reductions are mediated through surface states or a narrow intermediate band with energies located at about −0.4 eV. Reductions utilizing these surface states or band cannot occur at rapid rates until the Fermi energy of electrons in the interior of the electrode approaches the energy of the surface states or band energy at the surface since it would not be possible to replenish efficiently electrons consumed during a reaction. For an energy level located at −0.4 eV, this condition would be fulfilled at a potential of +0.4 V. An energy level located at −0.4 eV might also mediate electron transfer for TMPD$\cdot^+$ (depending on λ) but, because the magnitude of $W_{ox}(E)$ at −0.4 eV for TMPD$\cdot^+$ is much less than those for the previous three compounds, its reduction rate would be less at similar potentials. This intermediate energy level may not be efficient for carrying out oxidations, because a mechanism for rapidly removing electrons from this energy level to bulk SC may not exist. For a reduction, this level may be rapidly repopulated from the conduction band. For an oxidation, few vacancies are present in the valence band for electrons to drop into from this level. Electrons would have to be removed by thermal excitation into the conduction band which may be a slow process.

Recent investigations of the photoelectric processes in TiO_2 have indicated that there are a number of traps and energy levels located in the band gap.[17] Several of these levels have energies near that proposed for the intermediate energy level in this investigation. In addition, investigations of N_2O dissociation on TiO_2 have suggested the possibility of efficient electron transfer via surface donors.[18] Measurements at polycrystalline TiO_2 also indicate that significant numbers of donor centers may be located near the surface.[12] Ample precedent therefore exists for expecting possible participation of intermediate energy levels in electron transfer processes at TiO_2. Further support for an intermediate energy level comes from measurements of the variation of rate vs. potential. For reactions occurring solely via the conduction band, the rate should vary according to $\exp(-\alpha\Delta\phi_s/kT)$ with $\alpha = 1$.[19] Participation of surface states will decrease the potential dependence of the rate and show an α value less than 1. For thianthrene cation radical reduction, α was always less than 1 and was a function of potential, decreasing at increasingly negative polarization. Although these measurements may be somewhat questionable by our inability to compensate completely for internal resistance effects, the results are consistent with participation of an intermediate energy level.

Whether this intermediate level is band-like or corresponds solely to surface states is not known. However, surface donor centers are probably produced during the high temperature activation.[18] These donor centers are likely associated with oxygen vacancies or surface Ti^{3+} atoms.[18]

The presence of nonionized donor centers or traps and any associated relaxation phenomena can markedly affect the measured SC–electrolyte interface capacitance.[12] These effects include nonlinearity of Schottky–Mott plots and a frequency dependence of $1/C^2$.[1,20] In the present case, V_{fb} becomes more positive at higher frequency, indicating that, at high enough frequencies, relaxation phenomena become less important and the measured capacitance corresponds more closely to the space charge capacitance. Because of this, we do not feel that capacity measurements give an accurate value for the flat band potential and give only an estimate of donor density.

Compounds that have a significant overlap of $W_{red}(E)$ with the intermediate energy level should be oxidizable if vacancies or holes can be rapidly generated in this level. Illumination of the electrode with band gap light generates holes in the valence band which in turn can be filled by electrons from the intermediate level. The resulting holes at this energy can accept an electron from a solution species. The hole-electron pairs generated by illumination represent a nonthermodynamic distribution of carriers at the electrode surface. Oxidations can therefore occur at potentials negative of where they can thermodynamically occur. The product of *p*-benzoquinone reduction is oxidized at potentials considerably negative of its oxidation at platinum. Significant reoxidation apparently occurs negative of *p*-benzoquinone reduction since the height of the *p*-benzoquinone reduction wave decreases during illumination. In the case of *p*-benzoquinone, photooxidation is occurring at potentials where there is a downward bending of the bands. Normally a photooxidation will not occur unless the bands are bent in such a direction that the field of the space charge region will favor accumulation of holes at the electrode surface. For this reason, we find the photooxidation of *p*-benzoquinone anion to be unusual but offer no explanation as to its occurrence at these potentials. The photooxidation results of thianthrene are not conclusive. The failure to observe reduction of any photooxidized compound may either mean that no energy levels exist in the gap to mediate electron transfer for oxidation of thianthrene or perhaps more likely the thianthrene cation radical generated at the electrode may react with the products of solvent oxidation which occurs in the same potential region during illumination.

Capacitance measurements of TiO_2 with different crystal planes exposed to solution[21] suggested the possibility of observing different electrochemical behavior depending on the crystal plane one chooses to work with. We did not obtain any single crystal TiO_2 cut perpendicular to the a_2 axis with which to investigate this possibility. However, the results with the polycrystalline material, which should have all possible crystal orientations exposed to the solution, did not differ in any significant way with the single crystal results. This would suggest that, except for the differences observed for the capacitance measurements,[21] the electrode responses of the different crystal planes are nearly the same.

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Quantitative Study of Solvent Effects on Menshutkin Reaction between 1,4-Diazabicyclo[2.2.2]octane and (2-Chloroethyl)benzene, (2-Bromoethyl)benzene, and (2-Iodoethyl)benzene

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Abstract: By kinetic studies and product analysis, we have shown that the reaction between 1,4-diazabicyclo[2.2.2]octane on the one hand and (2-chloroethyl)benzene, (2-bromoethyl)benzene, and (2-iodoethyl)benzene on the other hand are Menshutkin quaternization reactions. By working in pure solvents and making use of the correlation method, the irregular behavior of protic solvents is shown. This is interpreted in terms of specific interactions between the protic solvents on the one hand and the halides on the other. There is a deactivation of the amine by formation of hydrogen bonded complexes with the protic solvents and a specific activation of the alkyl halides by these same protic solvents, all the more important as the halogen is more electronegative.

The influence of solvents on the rate of chemical reactions has been observed a long time ago. Attempts were made to express kinetic effects of the medium in terms of physical or thermodynamic properties of the solution.[1] Efforts which have been put forward to derive valid quantitative relationships are not satisfactory owing to oversimplifications. However, a "general" empirical solvent activity scale based on the results of a particular reaction has been put forward by some authors.[2] They deduced a relationship between ln k for a standard reaction in various solvents and ln k for the reaction under study in the same solvents. However, the activity scale shown was limited by the amplitude, e.g., the Ω values,[3] or mostly by specific influence of medium rather than physical effects, e.g., the Y values.[4] Nevertheless, under some conditions, it is possible to find with this activity scale a correlation which accounts fairly well for solvent effects.

The Menshutkin reaction has long been regarded as one of the best examples of solvent effects on the reaction rate. In this reaction, since ions are formed from neutral reactants, large increases in rate have been observed with increased polarity of the solvent.[5] So Drougard and Decroocq showed that it was possible to set up a solvent activity scale and chose as a standard reaction the quaternization of tripropylamine (TPA) by methyl iodide (MI) at 20°; the reaction was carried out in about a hundred solvents as well as in many binary mixtures.[6] In this scale, the solvent activity (S) was defined as

$$S = \log k_{2(\mathrm{TPA+MI})} \text{ at } (20°) \qquad (1)$$

where k_2 was the second-order rate constant in l. mol^{-1} min^{-1} in a given solvent for the reaction between TPA and MI. The relationship between S and the reaction rate is given by eq 2:

$$\log k_2 = (\log k_2)_{S=0} + RS \qquad (2)$$

where k_2 is the rate constant of a reaction in a solvent whose activity is S, R is a constant at a given temperature and is characteristic of the reaction. Thus, parameter R, which is supposed to be independent of the solvent, is a measure of the susceptibility of the reaction to the action of the solvent. There is a good linear correlation between the S values and solvent-sensitive absorption bands as well as kinetic data for various reactions.[6] In correlating a series of results, it became apparent that the solvent influenced the course of chemical reactions by nonspecific physical effects which depend on solvent polarity, polarizability, conjugated polarizability, and lastly on molecular structure and by specific chemical effects which depend on the solvation of the reactants.[7] Therefore, regular solvent effects must be distinguished from irregular ones. In some cases, reaction rates were only influenced by physical effects and gave perfect correlations; in others, there were specific reactant solvation effects. Protic solvents, for example, show an irregular behavior when they form hydrogen bonds with reactant species.

In this work, we analyze the solvent influence upon the Menshutkin reaction, particularly for protic solvents. The reactants chosen were 1,4-diazabicyclo[2.2.2]octane