The effect of hole acceptors on the photocurrent response of particulate TiO₂ anodes†

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The effect of different hole acceptors on the photocurrent response of particulate TiO₂ anodes was investigated. In all cases there was a significant increase in the photocurrent over that observed for the photooxidation of water. The photocurrent efficiency observed in the presence of hole acceptors followed the order: oxalate > formate > acetate > methanol. The order of efficiency of the hole acceptors does not correlate with reported free hydroxyl radical reactivity constants or with reported oxidation potentials for the substrates studied. Adsorption measurements made in the dark showed that oxalate was much more strongly adsorbed on the electrode surface than either acetate or formate. Impedance spectroscopy indicated an increase in the capacitance of the system due to the presence of oxalate, both in the dark and under illumination.

Introduction

Photoelectrochemical cells (PECs) incorporating nanocrystalline particulate TiO₂ electrodes have been employed for various applications including solar to electric energy conversion,1 electrochromic devices,2 and the photocatalytic destruction of aqueous organic pollutants.3,4 The so called Grätzel cell, which has shown solar to electric conversion efficiencies of 15% in overcast conditions, operates by indirect absorption of light (sensitisation), allowing use of visible wavelengths.1 Alternatively, direct absorption of light by nanocrystalline films may be used in a photovoltaic cell where photogenerated electron–hole pairs are separated kinetically e.g. the presence of an efficient hole scavenger in the electrolyte minimises direct charge carrier recombination in the film.5 In both cases only majority carriers are involved in charge transport in the film.6 Inorganic ions such as iodide7 and sulfide,5 and organic compounds including methanol and glycine8 have been reported to act as efficient hole scavengers. However, no detailed comparison of the relative efficiency of hole scavengers has been reported. Previous work at our laboratories using particulate TiO₂ electrodes showed that photocurrents in the presence of oxalate were up to 30 times those observed for the photooxidation of water.9 Whal et al. reported that the selective oxidation of methanol on particulate TiO₂ films resulted in a 20 fold increase in photocurrent over that observed for the photooxidation of hydroxide ions, and that the increase in current was due to faster hole transfer to methanol.10

In this paper we present the results of a recent study comparing the effect of different hole acceptors i.e. oxalate, formate, acetate, and methanol, on the photocurrent response of particulate TiO₂ electrodes in a two compartment PEC. The aim of this work was to determine if any correlation could be made between the photocurrent response and reported oxidation potentials, hydroxyl radical reactivity constants, or adsorption coefficients of the hole acceptors studied.

Experimental

TiO₂ photoanodes were prepared by the electrophoretic immobilisation of TiO₂ powder (Degussa P25, Degussa AG, Frankfurt, Germany) on Ti-4V-6Al alloy (2 × 2 cm², Shorts, Belfast, Northern Ireland), described previously.11 Electrical contact was made to the alloy using conducting epoxy (CW2400 Circuit Works, RS Components, Corby, UK) and a copper wire. The contact and any supporting substrate not coated with TiO₂ was coated with negative photoresist (Kodak, School of Electrical and Mechanical Engineering, UUJ). The photoresist was UV cured and provided a durable resistant insulating layer necessary to reduce interference from dark currents.

The electrolyte used throughout was 0.5 mol dm⁻³ potassium chloride (Aldrich, Gillingham, UK) and the hole acceptors used were sodium oxalate, sodium acetate, sodium formate (Aldrich) and methanol (Labscan Ltd., Dublin, Ireland). All were present at 5 × 10⁻³ mol dm⁻³ in the anode compartment, unless stated otherwise. All measurements were made in a Pyrex two compartment cell described previously.9 The anode compartment held the TiO₂ working electrode and a saturated calomel reference electrode. The cathode compartment held a platinum spiral counter electrode. Oxygen was removed from the anode compartment by oxygen free nitrogen, OFN, (BOC, Belfast, Northern Ireland) purging (blanketed during measurements) because it has been shown previously both by ourselves and other workers to be responsible for photocurrent quenching.7,12 The photoanode was illuminated through the wall of the reactor using a 150 W xenon arc lamp (Sage Analytical, Heywood, UK) with stabilised power supply (Applied Photophysics, London, UK). The light intensity (λ 300 to 400 nm) incident upon the electrode was measured using ferroxalate actinometry13 with a 300–400 band pass filter (Speirs Robertson, Beford, UK).

Linear sweep voltammetry, chronoamperometry and open circuit potential measurements were made using a Yecopel AEW2 potentiostat (Yecopel Scientific Ltd., Boldon, UK) with PC control. Short circuit photocurrents were measured using a Keithly multimeter with data logger (Elecroplan, Royston, UK). The time dependence of the dc photocurrent under
constant electrode polarisation was obtained with hand chopped light. All experiments were carried out using unbuffered electrolyte (0.5 mol dm\(^{-3}\) KCl) and the initial pH of the electrolyte in all cases was 7 ± 0.5. The temperature of the anode was thermostated to 20 ± 2 °C throughout. The incident light intensity was constant and determined to be 2.3 × 10\(^{-8}\) mol s\(^{-1}\) cm\(^{-2}\) (λ 300 to 400 nm).

In adsorption experiments the concentrations of the organic acids were determined by HPLC using an Aminex HPX-87H ion exclusion column (300 mm × 7.8 mm id, Bio-Rad, supplied by Alpha, Larne, Northern Ireland), a P2000 pump, AS1000 autosampler, LIS UV/VIS detector, and PC 1000 software by Alpha, Larne, Northern Ireland), a P2000 pump, AS1000 autosampler, LIS UV/VIS detector, and PC 1000 software (Thermo-Separation Products, Thermoquest UK, Manchester, UK). The conditions for HPLC were as follows: mobile phase was 10\(^{-3}\) mol dm\(^{-3}\) H\(_2\)SO\(_4\) at a flow rate of 0.6 cm\(^3\) min\(^{-1}\) : 20 μl injection loop for oxalate and 100 μl for formate and acetate: detection at λ 210 nm.

Ac impedance spectroscopy was carried out using an Autolab PGSTAT 20 Electrochemie (Windsor Scientific, Slough, UK). The starting potential was applied for 10 min followed by a potential scan with a 0.1 V step with 30 s equilibration at each potential. The amplitude of the sinusoidal wave was 5 mV and the frequency considered for the Cs value was 1000 Hz. The scan with a 0.1 V step with 30 s equilibration at each potential. Starting potential was applied for 10 min followed by a potential decayed slowly towards the dark potential. In the presence of acetate and formate the electrode adopted a steady negative shift in E\(_{fb}\) at pH 7 to be ~ 0.9 V at pH 11. This is close to the calculated E\(_{fb}\). When the light was turned off the negative potential decayed slowly towards the dark potential. In the presence of methanol E\(_{fb}\) was significantly positive of E\(_{fb}\). In the presence of acetate and formate the electrode adopted a potential similar to that observed for the electrolyte alone. However, in the presence of oxalate there was a significant negative shift in E\(_{oc}\) to ~ 1029 mV. When short circuit to the Pt counter electrode, in the oxygen saturated cathode compartment, the electrode immediately adopted the dark short circuit potential.

Open circuit photovoltage and short circuit photocurrent

The open circuit photovoltage (E\(_{oc}\)) of the electrode in the presence and absence of the hole acceptors was measured against the reference electrode. Results are shown in Table 1. Upon illumination in electrolyte alone, the electrode adopted a steady negative potential E\(_{oc}\) = −725 mV. This is close to the calculated E\(_{fb}\). The open circuit photovoltage and short circuit photocurrent density (j\(_{sc}\)) recorded when the TiO\(_2\) anode was short circuited, through an ammeter, to the Pt counter electrode in the O\(_2\)-saturated cathode compartment. The short circuit photocurrent response of the electrode in the presence of different hole acceptors followed the order: oxalate > formate > acetate > methanol > KCl only with ratios (j\(_{sc}/j_{sc(KCl)}\)) of 15 : 12 : 5 : 1.6 : 1. This is the same order as observed in the LSV experiments, however, the ratios of current response in the presence of hole acceptor to that observed in KCl only are significantly greater for oxalate and formate compared to those found with LSV.

Photocurrent–time behaviour

The study of the transient photocurrent–time behaviour frequently observed in photoelectrochemical cells is an interesting tool for the analysis of charge transfer mechanisms at the semiconductor electrolyte interface. The photocurrent–time response of the electrode was determined by chronoamperometry, under a constant pre-pulse potential, using hand chopped light. The response of the photosensitive electrode under fixed potentials, allowing separation of the faradaic and capacitive components. Alternatively one can use chronoamperometry to analyse the photocurrent–time response of the electrodes under fixed potentials, allowing separation of the faradaic and capacitive components.

<table>
<thead>
<tr>
<th>Hole acceptor (5 × 10(^{-3}) mol dm(^{-3}))</th>
<th>E(_{oc})/mV</th>
<th>E(_{fb})/mV</th>
<th>I(_{sc})/μA</th>
<th>j(_{sc})/μA cm(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl only</td>
<td>−725</td>
<td>−185</td>
<td>52</td>
<td>13</td>
</tr>
<tr>
<td>Methanol</td>
<td>−150</td>
<td>−67</td>
<td>84</td>
<td>21</td>
</tr>
<tr>
<td>Acetate</td>
<td>−680</td>
<td>−145</td>
<td>277</td>
<td>69</td>
</tr>
<tr>
<td>Formate</td>
<td>−754</td>
<td>−278</td>
<td>644</td>
<td>161</td>
</tr>
<tr>
<td>Oxalate</td>
<td>−1029</td>
<td>−258</td>
<td>808</td>
<td>202</td>
</tr>
</tbody>
</table>

Table 1 The open circuit photovoltage (E\(_{oc}\)), the short circuit photovoltage (E\(_{sc}\)), the steady state short circuit photocurrent (I\(_{ss}\)) and the short circuit photocurrent density (j\(_{sc}\)). The electrode area was taken as the geometric area.

Fig 1 LSV of TiO\(_2\) electrode in the dark and under illumination. KCl (0.5 mol dm\(^{-3}\)) was present as supporting electrolyte. SR 10 mV s\(^{-1}\). The anode was purged with OFN and the cathode with oxygen prior to sweep. All substrates were present at 5 × 10\(^{-3}\) mol dm\(^{-3}\). 1: electrolyte only; 2: electrolyte only, light; 3: methanol, light; 4: acetate, light; 5: formate, light; 6: oxalate, light.
electrode in the presence of the different hole acceptors (at 0.0 mV) is shown in Fig. 2. The initial photocurrent $I_{ph, in}$ is taken as the current directly after the light is switched on at time $t_0$ minus the dark current. The steady-state photocurrent $I_{ph, st}$ is given by the steady-state current, just prior to $t_2$, minus the dark current. $I_{ph, in}$ and $I_{ph, st}$ were measured, in the presence of the different hole acceptors, as a function of applied potential. Fig. 3 compares $I_{ph, st}$ as a function of applied potential in the presence of the different hole acceptors and for KCl alone. The same order of photocurrent response was observed as mentioned previously, but the ratio $I_{ph, st}/I_{ph, st}[KCl]$ was slightly higher for oxalate and formate compared to the ratios for acetate or those measured by LSV. $I_{ph, st}$ for KCl tended towards zero at around −300 mV, 400 mV positive of $E_{fb}$. For methanol and acetate $I_{ph, st}$ tended towards zero at around $E_{fb}$, yet $I_{ph, st}$ for oxalate and formate tended towards zero at potentials more negative than $E_{fb}$.

$I_{ph, in}$ and $I_{ph, st}$, in the presence of oxalate, are plotted against applied potential in Fig. 4. At negative potentials $I_{ph, in}$ and $I_{ph, st}$ were low, but surprisingly, were of equivalent magnitude. They began to separate at −600 mV where the $I_{ph, st}$ plateaued, yet the $I_{ph, in}$ continued to increase with increasing anodic bias until it plateaued around 0.0 mV. This behaviour is not typical and is, in fact, the reverse of a normal transient response. Fig. 5 shows the ratio $I_{ph, st}/I_{ph, in}$ as a function of applied potential, in the presence of hole acceptors and for KCl alone. Both KCl and methanol showed a typical response where the ratio tended towards zero around $E_{fb}$. The ratio approached unity near 200 mV $\Omega_s = 900$ mV. For acetate the ratio reached unity under lesser bandbending around −400 mV $\Omega_s = 300$ mV. For formate the ratio remained effectively constant at around 0.4, while for oxalate, mentioned above, the ratio reached unity at negative potentials at around $E_{fb}$ and then decreased to 0.4 at 0.0 mV remaining constant under conditions of high band bending.

Salvador measured the time current transients of single crystal TiO$_2$ in 1 mol dm$^{-3}$ Na$_2$SO$_4$ using hand chopped light. He reported that $I_{ph, in}$ extrapolates to zero near $E_{fb}$, yet the onset of the steady-state current $I_{ph, st}$ was about 450 mV positive of $E_{fb}$. Also the transient ratio $I_{ph, st}/I_{ph, in}$ increased exponentially with increasing bandbending, reaching a plateau very near unity for $\Omega_s \geq 1$ V and the critical band bending was 0.5 V i.e. the induced bandbending required to prevent surface recombination reactions.

The photocurrent–time behaviour measured for our electrodes do not follow the same pattern reported by Salvador. The main difference is that the decay time from initial to steady-state current is measured in 10’s of seconds rather than seconds or milliseconds, i.e. it is not transient. Similar behaviour was reported previously by Hagfeldt et al., for nanocrystalline TiO$_2$ films. A cathodic spike assigned to the reduction of oxidised species on the surface ($\text{OH}^-$) was not observed for our system. In our system the current was sampled at 7 times per second which may not be adequate to detect either a space charge anodic spike or a reductive cathodic spike.

Fig. 6 shows the current–time behaviour of the electrode for two concentrations of oxalate under conditions of high

![Fig. 2](image2.png)  
**Fig. 2** Photocurrent–time behaviour TiO$_2$ electrode in the presence of different hole acceptors recorded at 0.0 V (versus SCE). KCl (0.5 mol dm$^{-3}$) was present as supporting electrolyte. All organic substrates were present at $5 \times 10^{-3}$ mol dm$^{-3}$: 1, electrolyte only; 2, methanol; 3, acetate; 4, formate; 5, oxalate.

![Fig. 3](image3.png)  
**Fig. 3** Steady-state photocurrent as a function of applied potential for each of the hole acceptors and for electrolyte alone.

![Fig. 4](image4.png)  
**Fig. 4** The initial and steady-state photocurrent measured as a function of applied potential when oxalate was present in the anode compartment.

![Fig. 5](image5.png)  
**Fig. 5** Plot of the ratio $I_{ph, st}/I_{ph, in}$ as a function of applied potential in the presence of different hole acceptors and for electrolyte alone. The position of the estimated flat band potential $E_{fb}$ is shown for comparison.
bandbending $\Phi_b = 1.5$ V. At the higher concentration of oxalate there was no current decay following $t_0$ and the ratio $I_{ph, out}/I_{ph, in}$ is close to one. At high concentrations of oxalate the ratio was independent of the applied potential.

### Adsorption of hole acceptor

The photocurrent–time behaviour of the electrode in the presence of oxalate suggested that adsorption of oxalate to the TiO$_2$ surface may be a crucial factor determining the photocurrent. Langmuir–Hinshelwood (L–H) kinetic models are often used to describe the photocatalytic degradation of organic pollutants on TiO$_2$. The adsorption constant determined from kinetic studies is usually much larger than that obtained from dark adsorption isotherms.$^{17}$ It was found previously that $j_{ph}$ was directly proportional to the rate of oxidation of oxalate and that $j_{ph}$ measured over a range of initial oxalate concentrations did not obey the L–H model.$^9$ Therefore, the extent of adsorption of the hole acceptors, oxalate, formate, and acetate, onto the electrode surface, was determined in the dark. Assuming a simple Langmuir isotherm of the form

$$n^2 = \frac{n^2 b C_2}{1 + b C_2}$$

(1)

where $n^2$ is the number of moles of solute adsorbed per cm$^2$ of electrode surface (geometric), $n$ is the number of moles of adsorption sites per cm$^2$ of electrode surface, $C_2$ is the solute equilibrium concentration, and $b$ is the adsorption constant. At low concentrations $n^2$ was proportional to $C_2$ (Fig. 7) and the slope of the line is equivalent to $n^2 b$. All data showed a reasonable fit with $R^2$ values close to unity. Since $n$ is constant on the same electrode, then the slope $n^2 b$ is a measure of the relative extent of adsorption. The results are shown in Table 2. A reciprocal plot of the data gave a straight line fit but with negative intercept suggesting that simple Langmuir adsorption is not obeyed at higher concentrations of solute. Oxalate (Fig. 7.1) which is much more strongly adsorbed than acetate (Fig. 7.2) gives the highest photocurrent efficiency. However, acetate which is more strongly adsorbed than formate (Fig. 7.3) gives a lower photocurrent response than formate. Therefore, there is no direct correlation between the extent of adsorption and the order of photocurrent efficiency.

### Ac impedance spectroscopy

Impedance studies were carried out on the electrode system both in the dark and under illumination, in the presence and absence of oxalate. It was previously reported that illumination of nanocrystalline TiO$_2$ films resulted in an increase in the capacitance due to the build up of surface trapped holes.$^{18}$ Indeed, if this were the case, then the presence of a hole scavenger should lead to a decrease of this photocapacitive effect. Fig. 8 shows a Mott–Schottky type plot of the data. It is seen that in the presence of oxalate, a hole acceptor, the photocapacitance was increased compared to that measured in KCl alone. The value of $E_{fb}$ may be estimated from the intercept on the $X$-axis. In the dark, in the absence of oxalate, $E_{fb}$ was $\sim -0.8$ V (Fig. 8.1). When oxalate was added, $E_{fb}$ was shifted positive to $\sim -0.7$ V (Fig. 8.2) due to adsorption of oxalate. Upon illumination in the absence of oxalate there was an increase of the capacitance of the system and $E_{fb}$ was shifted positive to $\sim -0.5$ V (Fig. 8.4). It is possible that the generation of CO$_2$ within the particulate film, due to the photooxidation of oxalate, resulted in a lowering of the interfacial pH, which in turn, shifted the position of $E_{fb}$ more positive. These are preliminary results and require further investigation.

### Discussion

The films used in this work were prepared by the electrophoretic deposition of Degussa P25 TiO$_2$ on Ti-alloy. Degussa P25 is

![Adorption of hole acceptors on TiO$_2$ electrode over a range of concentrations.](image)

Table 2 Oxidation potentials $E_{p,a}$, second order rate constants for reaction of the ion with free hydroxyl radicals ($k_{OH}$), $I_{ph}$, the $pK_a$ values of the acids, and the adsorption data

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$E_{p,a}/V$</th>
<th>$k_{OH}/(10^{-6} \text{ dm}^{-1} \text{ mol}^{-1} \text{ s}^{-1})$</th>
<th>$I_{ph}/\mu A$ (at 800 mV)</th>
<th>$pK_a$</th>
<th>$n$ b$^{-2}$d$^{-1}$cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalate</td>
<td>0.8$^a$</td>
<td>7.7</td>
<td>1097</td>
<td>$pK_{a1} = 1.23$</td>
<td>14.0</td>
</tr>
<tr>
<td>Formate</td>
<td>0.3$^a$</td>
<td>3200</td>
<td>825</td>
<td>$pK_{a2} = 4.19$</td>
<td>1.70</td>
</tr>
<tr>
<td>Acetate</td>
<td>1.5$^a$</td>
<td>85</td>
<td>382</td>
<td>4.75</td>
<td>3.10</td>
</tr>
</tbody>
</table>

$^a$ In 0.5 M H$_2$SO$_4$ on a smooth Pt electrode.$^{28,29}$ Measured on a Pt electrode against a mercury–mercurous acetate reference electrode.$^{29}$ $^c$ Ref. 30.
70% anatase and 30% rutile, and the mean primary particle size is reported to be 21 nm.\(^{19}\) O’Regan et al, estimated the bandbending on 15 nm particles to be 0.3 mV under maximum depletion.\(^{16}\) Using their value we estimate the bandbending on 15 nm particles to be ~ 0.6 mV. The potential difference between the particle surface and the interior must be at least 50 mV in order for migration to dominate over diffusion of charge carriers.\(^{20}\) Thus, due to the small primary particle size, electron transport in the network of particles comprising the film is expected to be dominated by a gradient in the chemical potential of the electrons (diffusion) rather than by an electrical potential gradient (drift). The photocurrent response of these electrodes in the presence of different hole acceptors should then reflect the kinetics of charge transfer at the semiconductor electrolyte interface (SEI).

Sodergren et al.\(^{21}\) proposed models to describe the photoelectrochemical response of nanocrystalline electrodes in contact with electrolyte. In a particulate film the electrolyte is able to penetrate all the way to the back contact (supporting substrate). This will totally deplete all charge carriers, and there will be no bandbending. In these films the charge carriers are electrons, and the following assumptions are made by Sodergren et al.:

(i) Electron transport in the semiconductor occurs via diffusion.

(ii) The diffusion length of the electrons in the semiconductor is constant; recombination processes are assumed to be of first order.

A photoexcited hole is taken up by a hole acceptor in the electrolyte, and in order to produce a photocurrent the electrons must diffuse to the back contact. Since the particles in the film are surrounded by electrolyte, the electrons may recombine with e.g., an electron acceptor in the electrolyte, all the way to the back contact. Hence, the observed photocurrent quenching in the presence of \(\mathrm{O}_2\), an efficient electron scavenger. The rate of reaction of holes is assumed to be fast and the rate of reaction of electrons is assumed to be slow. However, where the rates of hole transfer are not the same, the concentration of electrons may be high due to electron injection, Sodergrens model cannot describe the photocurrent response of particulate films in the presence of different hole acceptors. The question still remains as to why such significant differences in the photocurrent response of our electrodes are observed due to the presence of different hole acceptors. The explanation must lie in the mechanism and rate of oxidation of the hole acceptor at the semiconductor surface.

Oxalate, formate and methanol\(^{22,23}\) have previously been reported to be current doubling agents. The oxidation of formate and oxalate occurs via hole capture to yield a \(\mathrm{CO}_2^-\) radical species with a reduction potential more negative than the conduction band of the \(\mathrm{TiO}_2\). The \(\mathrm{CO}_2^-\) radical may then inject a second electron into the conduction band to give \(\mathrm{CO}_2\). Harbour and Hair\(^{24}\) used spin trapping to identify radical intermediates in illuminated \(\mathrm{ZnO}\) suspensions. When formate or oxalate were present only the \(\mathrm{CO}_2^-\) radical was detected (no \(\mathrm{OH}^-\)). The \(\mathrm{CO}_2^-\) radical is known to arise from the reaction of hydroxyl radical with either formate or oxalate.

The primary oxidation of acetate on the other hand should not directly yield radical species capable of electron injection. Bard et al.\(^{25}\) investigated the reaction of organic acids with powdered \(\mathrm{TiO}_2-\)Pt. They found that in the case of acetic acid a one electron oxidation reaction could result in the decarboxylation of the molecule and called it the photo-Kolbe reaction:

\[
\begin{align*}
\text{CH}_2\text{COOH} & \rightarrow \text{CH}_3 + \text{CO}_2 \\
\text{(or } 2\text{CH}_2\text{COOH} & \rightarrow \text{C}_2\text{H}_6 + 2\text{CO}_2 + \text{H}_2) 
\end{align*}
\]

A one electron oxidation of acetate will result in the formation of a \(\mathrm{CO}_2\) molecule and a methyl radical, which can then either abstract a hydrogen from water or dimerise to form ethane.

Fermin et al.\(^{21}\) reported that the oxidation of organic species at the surface of single crystal \(\mathrm{TiO}_2\) occurs via surface-bound hydroxyl radical (\(\mathrm{OH}_s\)) generated by the photooxidation of water.\(^{23}\) The \(\mathrm{OH}_s\) intermediate is also involved in the recombination process and will capture electrons from the conduction band. However, efficient quenching of recombination in the presence of methanol and formic acid indicated that the \(\mathrm{OH}_s\) can capture electrons more readily from the organic species than from the solid. Lawless and Serpone\(^{26}\) reported that their results of a pulsed radiolysis study of \(\mathrm{TiO}_2\) were consistent with the interpretation that \(\mathrm{OH}_s\) is the major oxidant, while free hydroxyl radicals play only a minor role. If \(\mathrm{OH}_s\) is the major oxidising species some correlation between the observed photocurrent and reported free hydroxyl radical reactivity constants for the hole acceptors may be apparent. Table 2 shows the photocurrent observed in the presence of the different hole acceptors and reported free hydroxyl radical reactivity constants. There is no correlation between the rate constant for the hole acceptors and the photocurrent efficiencies observed. Also shown are reported photoelectrochemical oxidation potentials for the hole acceptors. Again no correlation is obvious between the oxidation potential and the order of photocurrent efficiency observed. Hoffman investigated the effect of different hole acceptors on the rate of \(\mathrm{H}_2\text{O}_2\) production in illuminated colloidal suspensions of \(\mathrm{ZnO}\)\(^{27}\) and reported the order of efficiency as follows: formate > oxalate > acetate > citrate. The order failed to match either the trends in the stability constants or the free hydroxyl radical reaction rate constants.

Formate gives higher photocurrent efficiency than acetate, yet acetate is more strongly adsorbed on the electrode surface (Table 2). Formate, however, has a much greater free hydroxyl radical reaction rate constant and is also reported to be a current doubling agent. In the case of formate, free hydroxyl radicals may play a more important role in the photooxidation process. The scavenging of free hydroxyl radicals in the electrolyte within the particulate film will result in higher photocurrents due to inhibition of surface recombination processes.

**Conclusions**

Significant differences in the photocurrent response of particulate \(\mathrm{TiO}_2\) electrodes were observed due to the presence of different hole acceptors in the electrolyte. The photocurrent efficiency followed the order: oxalate > formate > acetate > methanol > KCl only.

The films are comprised of nanosized particles, and charge separation may only be achieved as a result of differing rates of
electron and hole reaction at the surface. The order of hole acceptor efficiencies given by the measured photocurrent response does not correlate to either reported free hydroxyl radical reactivity constants or to reported oxidation potentials for the substrates studied. Dark adsorption studies showed that the extent of adsorption followed the order: oxalate >> acetate > formate.

Although the extent of adsorption does not directly correlate with the photocurrent efficiencies observed, it is almost certainly a crucial factor responsible for the high photocurrent response in the presence of oxalate. On the other hand adsorption to the surface is not a dominating factor where formate is concerned, but rather it is the relatively large free hydroxyl radical reactivity constant for formate which results in high photocurrent efficiencies. It was not possible to determine to what extent electron injection from radical intermediates contributed to the photocurrent response. Further work is being carried out in order to understand further the reasons for the differences in hole capture efficiency observed.

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