MECHANISM OF PHOTOELECTROCATALYTIC DEHYDROGENATION OF 2-PROPANOL ON A POLYCRYSTALLINE ZnO PHOTOELECTRODE

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Abstract—The mechanism of photoelectrocatalytic dehydrogenation of 2-propanol on a ZnO photoelectrode is re-examined. The effect of gaseous atmosphere is studied. The change of pH due to the reaction is followed under different experimental conditions. The larger part of the dissolution of ZnO occurs in the dark itself due to the solubility of ZnO. The photodissolution is comparatively small. 2-Propanol inhibits the photocorrosion slightly. H_2O_2 is detected in the electrolyte irrespective of the presence of 2-propanol. An electron transfer process followed by a free radical mechanism for the formation of H_2O_2 is proposed and discussed.

INTRODUCTION

In recent years there has been considerable interest in photoelectrosynthetic cells, especially photocatalytic cells. Most of these cells are based on semiconductor oxides and chalcogenides[1–5]. In a photocatalytic cell, the net electrolyte reaction has a negative free energy change and the activation energy for the forward reaction is provided in the form of optical energy. Syntheses of new chemical products are thus achieved at the expense of light energy. Among the several examples of photocatalytic reactions carried out in photoelectrosynthetic cells, Gerischer[6] and Morrison et al.[7–10] have made a detailed experimental study regarding the mechanism of reactions over a ZnO electrode. Both of these groups have reported the anodic photodissolution of ZnO in an inert electrolyte. When alcohols, aldehydes, amides, etc. are added to the electrolyte, it is found that the anodic photocurrent of the semiconductor electrode is doubled. Based on this observation, Morrison et al. proposed a current doubling mechanism[7–10]. Subsequently, similar studies were reported on several other semiconductor materials like TiO_2, CdS, GaP, etc. by different authors[1–6, 11, 12].

According to the mechanism proposed by Morrison et al.[7–10], photodissolution of ZnO is suppressed by added organic current doubling substrates. Holes formed by photons on an n-type semiconductor react with a current doubling substance R to give R^+, which then donates an electron to the conduction band and becomes R^{2+}. In a recent study, Fujishima et al.[13] questioned this mechanism and put forth a new mechanism where the ZnO corrodes further during the current doubling process. These authors conducted the studies using HCOONa as the current doubling agent.

The published information on the mechanism of formation of hydrogen peroxide suggests a need for

further investigation of this aspect. In the present experiments polycrystalline ZnO is used as the photoanode and 2-propanol as the current doubling agent. We have detected H_2O_2 in the system irrespective of the presence of the alcohols, contrary to the observation of Fujishima et al.[13]. In this paper, we present the quantitative data on the corrosion of the ZnO electrode and the pH changes noticed in the electrolyte during the electrode reaction.

EXPERIMENTAL

Electrode preparation

Different methods of preparation of the ZnO electrode have been tried in this laboratory. They are:

(1) painting a paste of ZnO over Pt and partially drying it;

(2) dipping Pt in colloidal ZnO solution and drying it;

(3) applying a paste of ZnO and a liquid crystal binder on a Pt foil;

(4) applying a flux like $CdCl_2$ and heating the material in nitrogen atmosphere at 500°C for 2 h after coating it over Pt foil. This is very similar to the method employed by Hodes et al.[14] for preparing chalcogenide electrodes;

(5) sintering a ZnO pellet at 1100°C for 3 h. Contact is made by silver epoxy and copper wire. Then the pellet is covered on all sides except one with epoxy resin.

All these electrodes were tried in the experiments and they did not show any difference in behaviour as far as the reaction mechanism is concerned. Some of these results have been published elsewhere[15–17]. The cell used for the present study can be represented as

Pt, Semiconductor oxide|0.1 M KCl, aq. org. substrate‖0.1 M KCl|Pt.

The cell consists of a two compartment Pyrex vessel with a bridge made of agar in a solution of saturated KCl and provision for bubbling the required gases through the electrolyte. A Spindler–Hoyer 200 W high pressure mercury arc lamp which is rich in 365 nm radiation (absorption maximum of ZnO) is used. ZnO is supplied by May and Baker, England and other reagents used are of the highest purity ensured by purification employing the standard methods. Peroxide present as impurity in 2-propanol is removed by passing the alcohol through a column of animal charcoal before each experiment. A Wenking potentiostat (model 70HP10) is used for potentiostatic experiments and a Keithley electrometer (model 610B) for current and voltage measurements. Experiments are carried out with and without applied bias. *Sce* is used as the reference electrode.

The method employed for the estimation of Zn^{2+} is that reported by Prasada Rao and Ramakrishna[18]. The Zn^{2+} in the solution is allowed to form tetrathiocyanato zincate(II) anion by adding potassium thiocyanate solution. On adding Rhodamine 6G solution to this, it forms a pink product which can be estimated by the spectrophotometric method, since this complex absorbs at 575 nm.

Presence of H_2O_2 is detected by adding titanium sulphate solution to the electrolyte after reaction. Presence of H_2O_2 produces a yellow colouration which helps to detect even 1 ppm of H_2O_2[19]. Acetone is detected by adding the electrolyte solution to alkaline salicylaldehyde and on heating to 50°C for 30 min, a reddish brown colour is observed indicating acetone[20].

RESULTS AND DISCUSSION

It is found that the nature and thickness of the electrode affect only the dark and final photopotentials but not the net photovoltage[15–17]. The trend of the current–potential curves for polycrystalline ZnO electrodes prepared by the different methods is almost the same as those reported by earlier workers[7–10, 13]. With addition of 2-propanol to the supporting electrolyte solution, the saturation photoanodic current increased. H_2O_2 and acetone were obtained as the reaction products.

The gaseous atmosphere in the photoelectrode compartment has an influence on the potential. ZnO electrodes are found to produce anodic photopotentials in nitrogen atmosphere. In an oxygen atmosphere, an initial cathodic photovoltage which gradually becomes anodic is observed (Fig. 1) but the final anodic photopotential is smaller in magnitude than that in nitrogen atmosphere. Oxidation of 2-propanol takes place at the ZnO electrode in nitrogen atmosphere also. The excited electron in the conduction band of ZnO can be expected to go to the counter electrode. But in the presence of oxygen, the surface oxygen may trap electrons from the conduction band of ZnO to form O_2^- on the surface. Such a trapping of electrons is possible on the surface if there is a distribution of surface states within the forbidden gap of the semiconductor, between the midgap position and the lower edge of the conduction band. Such a mechanism has been postulated by Sprunken et al.[21] for n-TiO₂
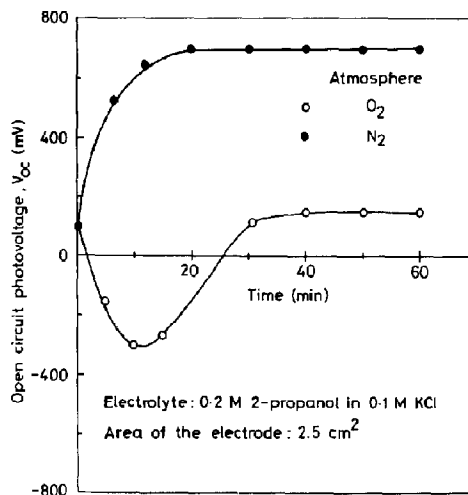

Fig. 1. Photovoltage *vs* time for ZnO electrode.

electrodes. These surface states enable the transfer of electrons and holes from the illuminated electrode to the solution (Fig. 2). Under such conditions, the photovoltage and photocurrent will drop to a negative value and O_2^- will transfer its extra electron to reducible species in solution. Hair and Harbour have reported the presence of O_2^- in solutions, when a semiconductor is illuminated in the presence of dissolved oxygen[22]. The O_2^- is unstable in aqueous media and can form HO_2^- radicals

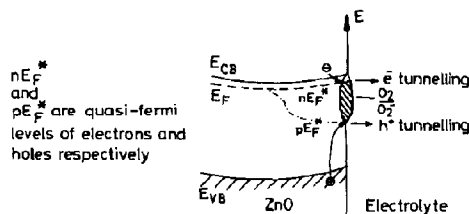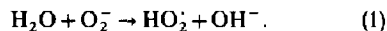$$H_2O + O_2^- \rightarrow HO_2^- + OH^-. \qquad (1)$$

Fig. 2. Energy scheme of photooxidation and photoreduction processes on ZnO electrode *via* surface state. Tunnelling of e^- and h^+ are shown by arrows.

These considerations are supported by the results of potentiostatic photocurrent–voltage measurements given in Fig. 3. In oxygen atmosphere the onset of photocurrent is shifted to more positive potentials. The initial cathodic photocurrent slowly changes to anodic current with a well defined transition potential. The final photocurrent at high anodic potentials is unstable and smaller in magnitude compared to that in a nitrogen atmosphere. This is more pronounced with $HCONH_2$ present in the system than with 2-propanol.

Contrary to the observations of Fujishima et al.[13] we have detected H_2O_2 in the anolyte with and without the addition of 2-propanol. Hauffe and Range also have reported the formation of H_2O_2 during photooxidation at a ZnO electrode[23]. Recently
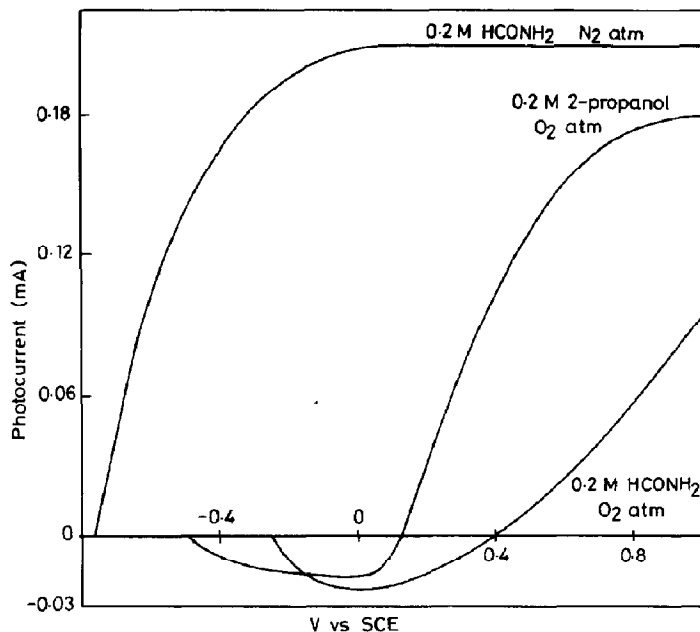
Fig. 3. Photocurrent *vs* voltage curve for ZnO electrode in N_2 and O_2 atmosphere.

Rao *et al.* have shown that illumination of ZnO or TiO_2 powders in water will produce H_2O_2 and H_2[24]. They have also shown a very good correlation between reactions in photoelectrochemical cells and reactions in photosynthesis in suspensions of the electrode material. In the present experiments, since in the absence of alcohol the quantity of H_2O_2 formed is very small, a large ZnO electrode was used, increasing the surface area more than ten times. Under such conditions, very small quantities of H_2O_2 could be detected. H_2O_2 is formed in the anolyte irrespective of the gas bubbled through (*ie* N_2 or O_2) the solution. The presence of strongly bound chemisorbed oxygen on the ZnO surface which may not be removed on bubbling nitrogen may be a possible reason for the formation of H_2O_2 in deaerated systems in the absence of alcohols.

The Zn^{2+} present in the anolyte under various experimental conditions has been estimated. The results are given in Table 1. The results show that
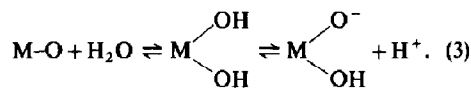
dissolution occurs in the dark itself and that contrary to previous reports[13] photodissolution is small compared to the spontaneous solubility of ZnO in the dark. Addition of 2-propanol suppresses the dissolution to a small extent and this implies that electron donation by 2-propanol is not fully utilized to eliminate the photocorrosion of ZnO (Table 1). This can be attributed to the kinetic parameters since whether or not photodissolution occurs depends to a large extent on the rates of the surface processes.

Changes in pH due to photoelectrochemical reactions

pH dependence of the flat band potential of the semiconductor oxides is well known. This pH dependence is because the oxide surface interacts with water by binding H^+ or OH^- depending on the acidic or basic character of the system,

$$M{-}O + H_2O \rightleftharpoons M^+{-}OH + OH^-, \qquad (2)$$

$$M{-}O + H_2O \rightleftharpoons M\begin{smallmatrix}OH\\ \\OH\end{smallmatrix} \rightleftharpoons M\begin{smallmatrix}O^-\\ \\OH\end{smallmatrix} + H^+. \quad (3)$$

Because of this charge separation, the potential drop in the Helmholtz double-layer varies with the pH. In a system where the pH is not kept under control by adding a buffer, the variation in pH can suggest the possible reaction mechanisms. The variations of pH in anolyte and catholyte under unbuffered conditions has been measured. In an unbiased system the extent of chemical reactions might be very small to give rise to detectable changes in pH. Therefore, measurements were made both with and without applied bias. The results are presented in Tables 2 and 3.

The pH of the anolyte increases in the dark itself and on subsequent irradiation remains unaffected in a nitrogen atmosphere. The nature of the bias is also not

Table 1. Concentration of Zn^{2+} in solution with and without 2-propanol

Experiment	Concentration of Zn^{2+} in solution	
	without 2-propanol ($\mu g\ ml^{-1}$)	with 2-propanol ($\mu g\ ml^{-1}$)
Cell in dark for 150 min	1.1	1.02
Irradiation for 30 min after deaeration for 30 min in dark	1.13	1.05
Irradiation for 105 min after deaeration for 30 min in dark	1.20	1.16
Irradiation for 270 min. after deaeration for 30 min in dark	1.28	1.16

Table 2. Variation of pH of anolyte (0.1 M KCl + 0.2 M 2-propanol) in N_2 atmosphere

No.	Experimental conditions	pH (± 0.05)
1	Anolyte before experiment	6.3
2	Anolyte after keeping in contact with the ZnO electrode (with/without bias); 5 h	7.65
3	Anolyte after irradiating for 1 h at 0.8 V bias	7.6
4	Anolyte after irradiating for 45 min at −0.2 V bias	7.65
5	Anolyte after irradiating for 1 h without any bias	7.65

Zn–CdCl$_2$ flux electrode. Reference electrode: sce. Temperature: 32°C.

Table 3. Variation of pH of catholyte (0.1 M KCl)

No.	Experimental conditions	pH (± 0.05)
1	Catholyte before experiment	6.3
2	Catholyte with an irradiated anode under under 0.1 V bias for 105 min (anodic current)	8.8
3	Catholyte with an irradiated anode under −0.25 V bias for 75 min (cathodic dark current and low anodic photocurrent)	6.4
4	Catholyte with an irradiated anode under −0.5 V bias for 90 min (cathodic current)	4.55

ZnO–CdCl$_2$ flux electrode. Reference electrode: sce. Temperature: 32°C.

reflected in the pH of the anolyte. The zinc oxide on dissolution interacts with the hydronium ions forming Zn^{2+} and water raising the pH of the medium. The dissolution of ZnO thus takes place in the dark itself (cf Table 1) and the pH of the anolyte moves towards a stable alkaline value. Thereafter the ZnO acts as a buffer and any further decrease of pH due to other chemical reactions (like oxidation of alcohol) would be compensated by dissolution of more ZnO or alternately by the neutralization of the proton released during the catalytic reaction by the O_2^- or OH^- present in the electrolyte. This process would affect either or both the pH and the Zn^{2+} concentration of the electrolyte.

The anolyte when saturated with oxygen traps the electrons to form O_2^-. This O_2^- reacts with the H^+ formed from the alcohol. Ordinarily O_2^- would react with water leaving the medium more basic. In the present conditions since O_2^- is just getting neutralised by the H^+ formed from the alcohol and the ZnO is prevented from reacting with H^+, the medium becomes slightly more acidic. To check this, the anolyte is initially saturated with oxygen and its pH noted before and after irradiation for 110 min at 1.0 V vs sce bias. The results are tabulated in Table 4. In the absence of alcohol there is very little chance for H^+ production in the solution, which means that on irradiation the pH is hardly affected. The experimental data (Table 4) supports this argument. With alcohol the pH shifted towards the acidic side whereas without alcohol the pH

Table 4. Variation of anolyte pH in O_2 atmosphere

No.	Experimental conditions	pH (± 0.05)
1	Kept under dark in O_2 atmosphere for 90 min*	7.35
2	The above solution is irradiated under +1.0 V bias for 110 min	6.85
3	Kept under dark in O_2 atmosphere for 90 min†	6.78
4	The above solution is irradiated under +1.0 V bias for 110 min	6.70
5	Kept under dark in O_2 for 90 min and irradiated under 0.1 V bias for 110 min (cathodic photocurrent)†	6.92

* 0.1 M KCl + 0.2 M 2-propanol.
† 0.1 M KCl.
ZnCO–CdCl$_2$ flux electrode. Reference electrode: sce. Temperature: 32°C.

shift was minimal. Under low anodic potential (+0.1 V vs sce) where the photocurrent is cathodic (Fig. 3) the pH shifted towards the basic side which can be accounted by the formation of O_2^- in the anolyte.

It is observed that the magnitude of the pH of the catholyte depends on the quantity of the current passed and the direction of the current. Under anodic current conditions the pH of the catholyte becomes basic and under cathodic current conditions, it becomes acidic. Without any bias, current being very small, no observable change is noticed in the pH of the catholyte.

Since the reduction potential of p-benzoquinone is similar to that of O_2, a dilute alcoholic solution of p-benzoquinone is added to the catholyte. During the experiment, the colour of the solution changes to brownish yellow. The uv-vis spectra of this yellow substance shows that p-benzoquinone (λ_{max} in CH_3OH solution = 243 nm) forms quinhydrone (λ_{max} in CH_3OH solution = 294, 242 nm) during the experiment. This is analogous to the formation of O_2^- from O_2. The pH of this solution also turned less acidic (from 4.38 to 6.95).

These results suggest an ionic reaction in the system involving electron-transfer followed by a secondary free radical mechanism which produces H_2O_2 as one of the products. To check this, a well known quencher, namely, acrylonitrile, is added to the anolyte. The photocurrent dropped from an initial value of 0.32 to 0.14 mA (at +0.25 V bias vs sce) on adding acrylonitrile. In the course of 50 min it again dropped down to 0.045 mA. On closely examining the irradiated electrode, it is found that the irradiated portion turned yellow with a coating of a polymeric substance over ZnO. Without 2-propanol also, the added quencher produced the same colouration (polymer) on the electrode. Taking into consideration the formation of H_2O_2 even in the absence of alcohol, the quenching experiment would suggest that a free radical reaction is taking place in the cell whether alcohol is present or not. In the photocatalytic oxidation of 2-propanol over ZnO suspensions, several workers [25, 26] have suggested a free radical mechanism. It is also possible for the acrylonitrile to accept an electron from another ionic species generated in the electrode

reaction and quench the subsequent reaction steps. This would curtail the possibility of electron-transfer to the electrode making the photocurrent smaller.

With 2,6-ditertiary butylphenol, another well known quencher which can also donate an electron by getting itself oxidized, the situation is different. This substance acted as a competitor for the current enhancing reaction. This quencher underwent reaction by itself over ZnO and could not suppress the current in any way. Therefore it is reasonable to believe that acrylonitrile is quenching the reaction by the abstraction of an electron whereas the phenolic substance abstracts the electron and continues to get oxidized. The free radical process leading to the formation of H_2O_2 is purely a solution reaction which cannot necessarily be a part of the photocurrent generating process.

Mechanism

In the light of all these observations, the following mechanism is suggested in the present system.

(a) Electrode dissolution in the dark. ZnO dissolves in water as

$$ZnO \xrightarrow{H_2O} Zn(OH)_2. \qquad (4)$$

Because of this solubility the pH of the solution increases as described in the previous section.

(b) Photoreactions in the anodic compartment. The generation of photocurrent can be represented by

$$ZnO \xrightarrow{h\nu} ZnO^* \xrightarrow[\text{to Pt cathode}]{-e} ZnO^+. \qquad (5)$$
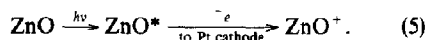
Equation (5) represents the production of photocurrent without added alcohol. Continuation of this process eventually leads to ZnO dissolution as Zn^{2+} in the electrolyte.

In an electrolyte containing 2-propanol, the alcohol can get chemisorbed over ZnO as shown in step (6).
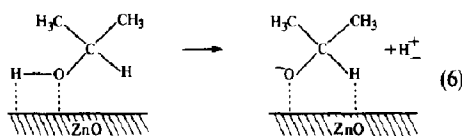

This is in accordance with the model proposed by Wolkenstein[27]. The O–H bond cleaves followed by the removal of H^+. Since corrosion is not enhanced in the presence of alcohol the separation of the hydrogen at this stage is unlikely to involve removal of an electron from the zinc oxide. Adsorption and decomposition of 2-propanol in this mode (ie the O–H bond cleavage as the first step) has been suggested by Koga et al.[28] also on the basis of ir and kinetic data.

The anion, $(CH_3)_2 CHO^-$ can lose one more hydrogen giving rise to acetone and the formation of a hydrogen atom.

$$ZnO^+ + H^- \rightarrow ZnO + H^\cdot. \qquad (8)$$
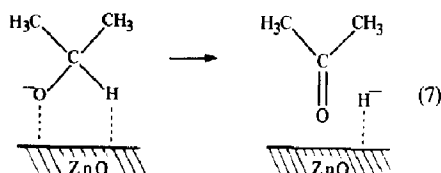
Reaction (8) reduces the photocorrosion reaction to a small extent (see Table 1). The other major reactions of H^- are represented by (9) and (10). The H^- produced in (7) can give an electron to the ZnO photoelectrode thus promoting the current enhancing reaction,

$$H^- \xrightarrow{ZnO} H^\cdot + e. \qquad (9)$$
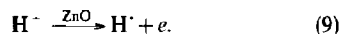
This is more favoured as H^- at the end of step (7) will still be in the adsorbed state. In the presence of a quencher like acrylonitrile H^- may give away the electron to the added acrylonitrile. H^- can also react with water,

$$H_2O + H^- \rightarrow H_2 + OH^-. \qquad (10)$$
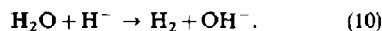
H_2 evolved as per the step (10) is not however detected, perhaps due to the very small amounts involved and the possibility of the adsorption by the Pt support of the electrode.

H from steps (8) and (9) can form H_2O_2 by a free radical reaction in solution via HO_2 radicals making use of the small quantities of O_2 and O_2^- formed by electron abstraction from the electrode. This mechanism is in agreement with the detected products, viz. acetone and H_2O_2.
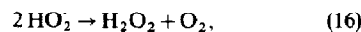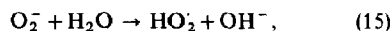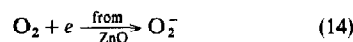
Other reactions are

$$OH^- + H^+ \rightarrow H_2O \qquad (11)$$

$$ZnO + 2p^+/2H^+ \rightarrow Zn^{2+}(aq) + H_2O/O. \qquad (12)$$
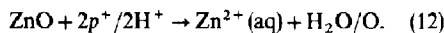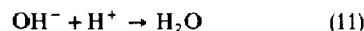
Step (12) explains the small amount of photocorrosion.

An alternative path for the formation of $(CH_3)_2CO$ is

$$(CH_3)_2CHOH \rightarrow (CH_3)_2C=O + 2H^+ + 2e. \qquad (13)$$
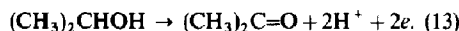
This, in the present case, is not likely because the presence of $2H^+$ in the system would be expected to increase the amount of corrosion during illumination at least to a small extent by the reaction of H^+ on the ZnO lattice, or it would be expected to cause a decrease in the pH. In the present experiments the pH is alkaline and the photocorrosion less in the presence of alcohol.
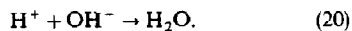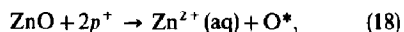
The possible cathodic reactions are

$$O_2 + e \xrightarrow[ZnO]{\text{from}} O_2^- \qquad (14)$$

$$O_2^- + H_2O \rightarrow HO_2^\cdot + OH^-, \qquad (15)$$

$$2 HO_2 \rightarrow H_2O_2 + O_2, \qquad (16)$$

$$H_2O_2 \rightleftharpoons \ddot{O}H + \ddot{O}H. \qquad (17)$$

In the study of the reaction of sodium formate on ZnO Fujishima et al.[13] had ruled out the possibility of H^+ reacting with ZnO (equation (12)). Even though

we have no conclusive proof to support the suggestion made by Fujishima *et al.*[13] our results strongly point to a preferential reaction of the H^+ with OH^- in solution.

The following scheme corresponds to Fujishima *et al.*'s mechanism, as applied to 2-propanol,

$$ZnO + 2p^+ \rightarrow Zn^{2+}(aq) + O^*, \qquad (18)$$

$$O^* + CH_3-\overset{\underset{\displaystyle |}{O^-}}{CH}-CH_3 \rightarrow (CH_3)_2CO + OH^-, \qquad (19)$$

$$H^+ + OH^- \rightarrow H_2O. \qquad (20)$$

This scheme does not explain the formation of H_2O_2 and also the observed suppression of the photodissolution of ZnO and the changes in pH.

CONCLUSION

The solubility of ZnO in the dark and the comparatively small photodissolution are established. The study of pH change in the PEC cell helps to understand the mechanistic route of the chemical reaction. Even in the dark, it is found that the pH increases. Increase in pH of the catholyte and reduction of added quinone to hydroquinone suggests clearly the possibility of the formation of O_2^- in the catholyte. The secondary alcohol undergoes an ionic electron transfer reaction followed by a free radical mechanism.

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