

**Short communication**

**PHOTOELECTROCHEMICAL REACTIONS OF SODIUM PROPIONATE  
OVER POLYCRYSTALLINE ZnO**

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The search for photocatalytic systems for the utilization of solar energy has brought to light several new reaction paths resulting in the production of  $H_2$ ,  $H_2O_2$ , hydrocarbons or other valuable energy-rich substances using solar energy [1–6]. Zinc oxide powder suspended in a solution containing reactants absorbs light and promotes electron-transfer reactions. In many of these reactions dissolved oxygen plays a crucial role via the superoxide anion [5–7]. In this note we wish to report the results of our studies on the photoelectrochemical and photocatalytic reactions of sodium propionate in the presence of polycrystalline ZnO, an n-type semiconductor oxide (band gap 3.2 eV; absorption maximum 365 nm).

Zinc oxide (May and Baker) was used as received for these studies. For photoelectrochemical (PEC) studies ZnO pellet electrodes were prepared by attaching the sintered pellet to a copper wire with an indium–gallium alloy and covering all sides except the one to be illuminated with epoxy resin.

An aqueous solution of 0.2 M sodium propionate (Riedel) and 0.1 M potassium chloride was used as the electrolyte for PEC studies. The light source was a Spindler–Hoyer 200 W high-pressure mercury arc lamp. The light intensity was  $3.2 \times 10^{-5}$  mol photons  $min^{-1}$ . Reaction cells were made of Pyrex glass. A Wenking potentiostat (Model 70HP10) was used for PEC studies. Voltage and current measurements were made with a Keithley 610B electrometer, with a SCE serving as the reference electrode.

For photocatalytic studies 1 g of ZnO was kept suspended in 80 ml of water by a magnetic stirrer and irradiated. Cold water was circulated around the reaction cell to maintain the system at 10°C. The solution was saturated with oxygen before irradiation and the cell kept airtight throughout the irradiation. To identify the gaseous products formed and to study the effect of gases on the reaction, the required gases, purified by standard methods, were bubbled through the solution while irradiating. The gas outlet was connected to a trap containing  $Ba(OH)_2$  solution to detect any  $CO_2$  produced during the reaction. Hydrogen peroxide was detected by the yellow coloration developed on addition of titanium sulphate to the experimental solution.

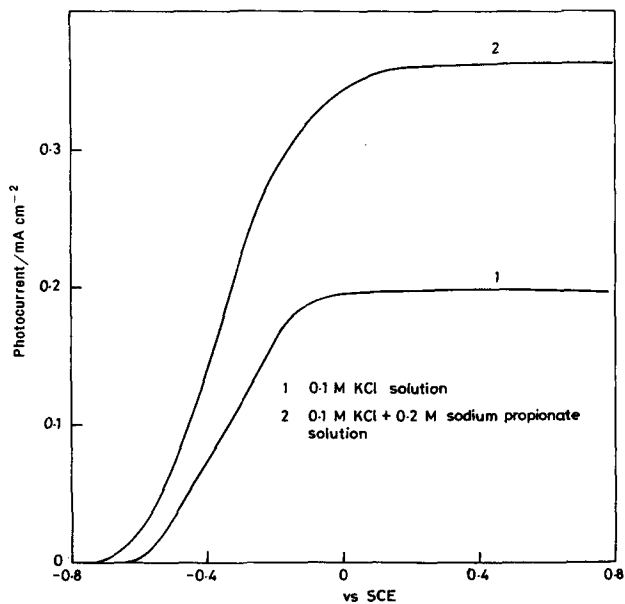


Fig. 1. The current-potential curve for a ZnO photoanode in nitrogen atmosphere under illumination.

Sodium propionate behaved as a typical current-doubling substrate. The  $I$ - $V$  characteristics of the cell before and after adding sodium propionate are shown in Fig. 1. The dark current was negligible (of the order of  $0.1$ – $1 \mu\text{A cm}^{-2}$  in the

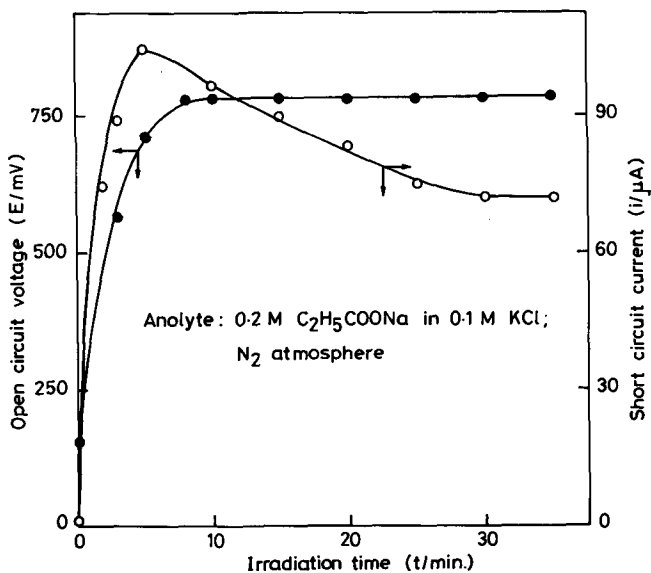


Fig. 2. Plot of open-circuit voltage and short-circuit current against irradiation time.

potential range scanned). The variation of open-circuit photovoltage and short-circuit photocurrent with time is shown in Fig. 2. The open-circuit photovoltage reached a maximum value and remained stable on irradiation, whereas the short-circuit photocurrent after reaching the maximum gradually falls back to a lower value and slowly levelled off. On switching off the light, both the open-circuit voltage and short-circuit current dropped to the dark value (dark current was negligible).

The initial rapid rise and subsequent fall in the short-circuit photocurrent may be due to several reasons. One of them could be that after the initial emptying of electron traps in the space-charge layer the current is mainly dependent on the reactivity of holes towards the oxidizable species. Further, the band bending decreases on illumination, reducing the electron-hole separation. A third reason for this behaviour can be the photocorrosion of the ZnO electrode.

In order to study the photoelectrochemical reactions nitrogen was bubbled through the anode compartment throughout the experiment. In both the photoelectrochemical and photocatalytic systems  $\text{H}_2\text{O}_2$  and  $\text{CO}_2$  were produced during irradiation. On addition of 2,4-dinitrophenylhydrazine reagent to the experimental solution to which dilute HCl was added to dissolve the zinc oxide, a precipitate was obtained. This precipitate, which is a mixture of hydrazone derivatives, was dissolved in ethyl alcohol and subjected to TLC analysis and subsequent separation by column chromatography (adsorbent: silica gel; eluent; hexane, ethyl acetate mixture). Four products were separated, recrystallized and identified by melting-point and NMR and UV-visible spectra. The products were acetaldehyde (major product), diethyl ketone (minor product), acetone (extremely small quantities) and unidentifia-

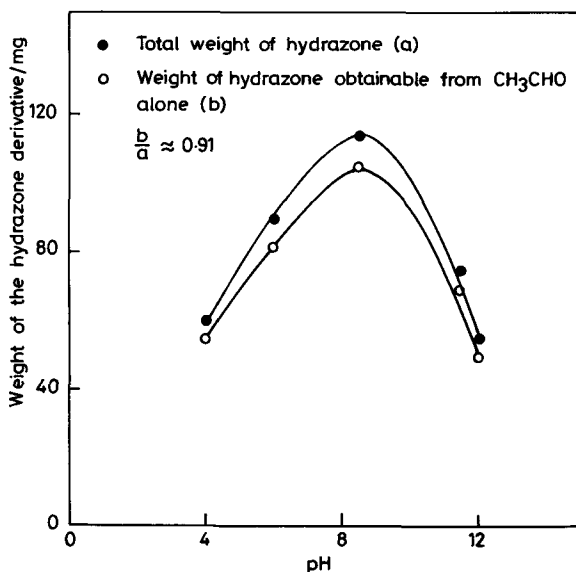


Fig. 3. Effect of pH on the product formation in a ZnO photocatalytic system.

ble carbonyl compounds (trace amounts). Gas chromatographic analysis of the filtered irradiated solution confirmed the presence of acetaldehyde and acetone. With the available columns diethyl ketone and water could not be distinguished.

The products were found to be the same for both the PEC and photocatalytic systems. A ZnO particle in suspension behaves as a PEC microcell over which a catalytic reaction takes place.

It was found that when N<sub>2</sub> is bubbled through the solution in a photocatalytic cell, no product was formed even after 4 h of irradiation. The maximum yield of products was obtained when the solution was saturated with oxygen. Without any gas being bubbled the amount of the products formed was less, showing that dissolved oxygen is necessary for the reaction.

In a PEC cell, for the reaction to be effective, the presence of N<sub>2</sub> in the anolyte and O<sub>2</sub> in the catholyte is required. The presence of O<sub>2</sub> in the anolyte reduces the anodic photocurrent. This behaviour has also been noticed in studies with other substrates and has been explained on the basis of the formation of O<sub>2</sub><sup>-</sup> through a surface state on the photoelectrode [8–10]. The excited electrons, instead of moving towards the counterelectrode through the external circuit, tunnel through a surface state to the dissolved oxygen to form O<sub>2</sub><sup>-</sup>. Tunnelling through the surface state simultaneously increases the rate of electron–hole recombination and retards the catalytic reaction on the surface. Tunnelling of electrons and the higher rate of electron–hole recombinations, in turn, suppress the anodic photocurrent.

The effect of pH on the product formation in a photocatalytic system is represented in Fig. 3. The pH of the solution without the addition of acid or alkali is 8.5. The pH was adjusted with the addition of 1 mM HCl or 1 mM NaOH. The ketone and the aldehyde products were converted into their corresponding hydrazone derivatives and weighed. In a separate set of experiments the amount of CH<sub>3</sub>CHO formed at different pHs was estimated by gas chromatography. The quantity of the product was found to be proportional to the total weight of the hydrazone derivatives (Fig. 3), the ratio being approximately 0.91. From the figure it is evident that an increase or decrease in pH from the original value inhibits the catalytic reaction.

On the thermal reaction of propionic acid over metal oxides, diethyl ketone is the sole product. In the photocatalytic system using zinc oxide, diethyl ketone is a very minor product and the major products are CO<sub>2</sub>, H<sub>2</sub>O and CH<sub>3</sub>CHO.

Further study is needed to establish a reaction mechanism. The O<sub>2</sub><sup>-</sup> ion is probably involved in the reaction, as suggested for similar systems by Fujihira et al. [5]. These photocatalytic studies demonstrate the possibility of unconventional reaction paths under the influence of light in the presence of a catalyst.

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## REFERENCES

- 1 I. Izumi, F.R.F. Fan and A.J. Bard, *J. Phys. Chem.*, 85 (1981) 218.
- 2 A.J. Bard, *J. Phys. Chem.*, 86 (1982) 172.
- 3 Y. Oosawa, *J. Chem. Soc., Chem. Commun.*, (1982) 221.
- 4 M.V. Rao, K. Rajeshwar, V.T.P. Verneker and J. Bubow, *J. Phys. Chem.*, 84 (1980) 1987.
- 5 M. Fujihira, Y. Satoh and T. Osa, *J. Electroanal. Chem.*, 126 (1981) 277.
- 6 T. Inoue, A. Fujishima, S. Konishi and K. Honda, *Nature*, 277 (1979) 637.
- 7 T. Kanno, T. Oguchi, H. Sakuragi and K. Tokumaru, *Tetrahedron Lett.*, 21 (1980) 467.
- 8 H.R. Sprunken, R. Schumacher and R.N. Schindler, *Ber. Bunsenges Phys. Chem.*, 84 (1980) 1040.
- 9 K.R. Thampi, T.V. Reddy, V. Ramakrishnan and J.C. Kuriacose, *Electrochim. Acta*, in press.
- 10 T.V. Reddy, V. Ramakrishnan and J.C. Kuriacose, *Indian J. Chem.*, in press.