



ZINCOXIDE PHOTO ELECTRO CHEMICAL CELL IN THE PRESENCE OF N-METHYL FORMAMIDE

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ABSTRACT:

ZINCOXIDE(ZnO) is an n-type semiconductor which may be used as photo sensitive electrode and photo catalyst in the presence of organic substrates. ZnO photoelectrochemical (PEC) cell is constructed in the presence of N-methyl formamide (NMF). In oxygen atmosphere, ZnO electrode produces cathodic photocurrent which is attributed to the reduction of O₂ and anodic photocurrent is due to oxidation of NMF in the presence of N₂. A suitable mechanism is proposed for the electrode reactions.

Keywords: PEC CELL, ZnO, NMF, PHOTOVOLTAGE, PHOTOCURRENT

INTRODUCTION

The annual flux of solar energy falling on the earth is about 1.2×10^{21} Kcal.[1]. A large part of this (33%) is lost due to reflection by the atmosphere and the earth's surface. The rest of the energy is absorbed by the atmosphere (17%), oceans and seas (33%) and land (15%). Of the energy absorbed, only about 6×10^7 Kcal./year ($7 \times 10^{-4}\%$) is converted into chemical energy via photosynthesis in plants and by micro organisms. However, only a small portion of this converted energy is utilized by mankind.

For the efficient utilization of solar energy that is available it is necessary to develop suitable methods for its storage. The photochemical conversion of solar energy into either electricity or chemical fuel is one of the most attractive pathways. The first observation of photoeffect at

a metal or semiconductor electrolyte junction was reported by Becquere [2]. A practical use for energy storage in the form of production of hydrogen from water was realized by Fujishima and Honda [3]. Since then extensive investigations have been carried out all over the world in the area of photochemical synthesis of energy rich compounds and photochemical decomposition of water.

Systems without semiconductors are found to be less efficient due to poor separation of products and reactants and occurrence of thermal back reactions between the products [4]. In the presence of semiconductors, the absorption of reactants on semiconductors and participation of electronic states of the semiconductor makes the system more efficient.

Usually the reactions in particulate systems and in PEC cells are compared on the basis of the products formed. In most of the cases the products are the same for both the systems and each particle of the semiconductor in the particulate system is treated as a micro PEC cell.

The study of PEC cells gained momentum with the first report of Fujishima and Honda [3] relating to the photo-electrochemical decomposition of water at an n-TiO₂ electrode illuminated by ultraviolet light. In 1975 Gerischer[5] showed the use of PEC cells for conversion of solar energy to electricity using reversible redox systems as the electrolytes.

An understanding of the process occurring

inside the semiconductor on absorption of light and the charge transfer reactions that take place at the surface of the semiconductor in contact with the electrolyte is necessary for devising PEC cells for energy conversion.

Using semi conductor materials like ZnO, TiO₂, ZnO in the construction of PEC Cells received considerable attention. Any semi conductor to be effective in a PEC cell must be chemically inert and make use of solar energy in the visible region. ZnO is an n-type semi conductor with a band gap of 2.7 eV. This corresponds to utilization of 11.8% solar energy. ZnO is reported (1) as a stable semi conductor for electrolysis of water in the presence of light. Photo catalytic activity of ZnO is also reported (2).

In the present study ZnO is used as a photo electrode in a PEC cell consisting of NMF Aqueous solution as electrolyte. Photo voltages and photo currents are measured. ZnO in the powder state is used as photo catalyst and the products are identified.

EXPERIMENTAL

PEC cell is constructed using polycrystalline ZnO paste. A thin layer of ZnO is deposited on a platinum foil and used as photo electrode. A platinum foil is used as counter electrode. A 1500W halogen lamp is used as light source. Electrolyte solution is a mixture of 0.1M KCl and 0.1M NMF.

ZnO,Pt/0.1 M NMF//0.1 M KCl/Pt
0.1 M KCl

here diagram to be inserted

RESULTS AND DISCUSSION

The sign of the open circuit voltage is found to depend upon gaseous atmosphere present at the electrode. In the absence of light the voltages are more positive in N₂ than in O₂. PEC cell produces a negative photo voltage and cathodic current in the presence of visible light and O₂. In the presence of N₂ a positive voltage is developed and anodic current is noted (table.1). If N₂ atmosphere is not maintained properly, the adsorbed O₂ on ZnO electrode surface initially produces cathodic current and then anodic current as shown in (Fig.1 & 2).

Table 1-Effect Of Gaseous Atmosphere On Photo Voltage And Photo Current

Electrolyte: 0.1 M NMF in 0.1 M KCl (40ml)

Area of the electrode: 3 cm²

Light source: 1000 watt halogen lamp

| Gaseous atmosphere at | | Open circuit photo-Voltage (mV) | Short circuit photo current (μA) | Nature of the photo-current |
|-----------------------|-------------------|---------------------------------|----------------------------------|-----------------------------|
| ZnO Electrode | Counter Electrode | | | |
| O ₂ | O ₂ | -150 | 3.1 | Cathodic |
| O ₂ | N ₂ | -140 | 2.9 | Cathodic |
| N ₂ | O ₂ | +45 | 0.5 | Anodic |
| N ₂ | N ₂ | +43 | 1.0 | Anodic |

Effect of intensity of light on photo voltage in O₂ atmosphere and 0.1M KCl and 0.1M N-Methyl formamide is studied. The photo voltage increases with light intensity and reaches a limiting value. Photo voltage is maximum around 360 nm, which corresponds to the band gap of ZnO (3.2 eV).

The plot of photovoltage verses log of light intensity is linear (Fig 3) which shows that ZnO behaves as a semiconductor (3). The generation of anodic photo current is due to oxidation reaction. In the present case cathodic photocurrent is observed only in the presence of oxygen. When O₂ is replaced by N₂ gas only anodic photo current is generated. Hence, cathodic photo current is due to reduction of O₂ to O₂⁻. Many Authors (8-10) observed similar effects on semi conductors. The super oxide Ion O₂⁻ is a good nucleophile and can react with carboxyl compounds (9). The O₂ reacts with N-methyl formamide to give CO₂ and CH₃.NH₂. CO₂ is identified at the electrode. However, CO₂ is not identified in the presence of N₂.

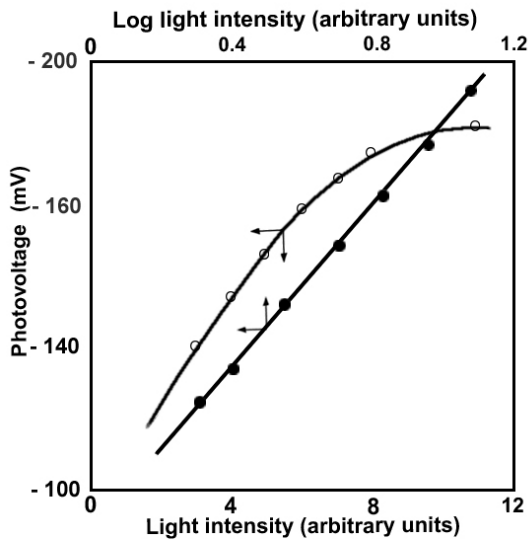
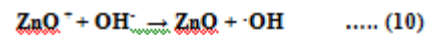
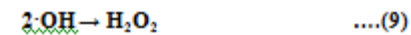
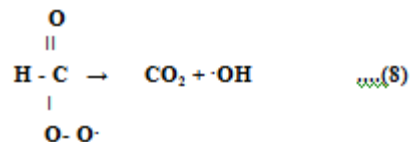
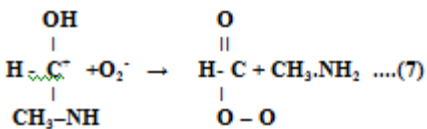
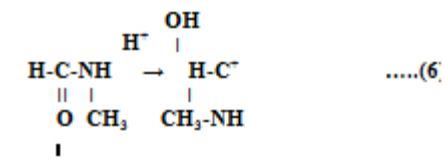
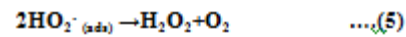
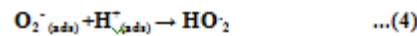
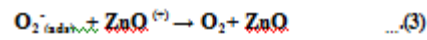
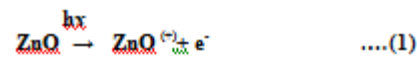


Fig3-Effect of intensity of light on photo voltage in oxygen atmosphere

Based on the experimental observations and the product analysis, a mechanism is proposed as given below. In reaction (2) the excited electrons in the conduction band flow to the surface of the electrode to react with adsorbed O₂ to give O₂⁻ and is responsible for the generation of cathodic photocurrent. The initial steep increase in photocurrent (Fig.3) is due to the availability of surface oxygen to react with the electrons as soon as illumination is started. The subsequent decrease may be due to poor electron hole separation and the oxidation of O₂⁻ radical by valence band holes (reaction 3). Detection of H₂O₂ provides additional evidence for the formation of O₂⁻ (12).

The other products, CO₂ and CH₃.NH₂ are formed only in the presence of oxygen and under illumination. Hence the O₂⁻ is expected to react with DMF to give CO₂ and CH₃.NH₂ as shown. Protonation of NMF (reaction 6) is well known in acidic medium and this facilitates O₂⁻ attack on the carbonyl carbon of the NMF.

The anodic nature of photocurrent in nitrogen



When the electrode is in nitrogen atmosphere, the electrons that are excited to the conduction band flow into the bulk of the semiconductor to produce anodic photocurrent. The photocurrent increases initially, attaining a stable value and then decreases slowly. Initially there is a greater amount of band bending which efficiently separates photoproduced holes and electrons. As the illumination progresses, the separation becomes less efficient due to decrease in band bending, resulting in recombination of electrons and holes. Hence the anodic photocurrent after reaching a maximum value starts decreasing.

It has not been possible to completely eliminate either oxidation or reduction at the electrode in a particular gaseous atmosphere. Both reactions can take place simultaneously and whichever dominates decides the sign of the photovoltage. In oxygen, reduction takes place

by conduction band electrons along with the oxidation of NMF by valence band holes during illumination (14). But the rate of reaction with holes is very slow while the reduction of oxygen is faster. Hence negative photovoltage dominates in this case. In nitrogen the presence of minute amounts of oxygen, like surface oxygen leads to an initial generation of negative photovoltage which gradually becomes positive. Only prolonged purging of the electrolyte with nitrogen completely eliminates negative photovoltage (Fig.2).

CONCLUSION

Development of photoelectrochemical cells less sensitive to air and not requiring hermetic seals will decrease the fabrication costs as well as the technological problems. One can consider the ZnO based photoelectrochemical cell which is not sensitive to air. But the efficiency of such a cell is very low. Investigations are in progress to improve the cell efficiency and electrode stability.

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