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Tungsten Trioxide (Wo_3) Based Photo Electro Chemical (Pec) Cell In The Presence of N-Methyl Formamide

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Abstract--- *TUNGSTEN TRIOXIDE (WO_3) is an n-type semiconductor which may be used as photo sensitive electrode and photo catalyst in the presence of organic substrates.WO_3photoelectrochemical (PEC) cell is constructed in the presence of N-methyl formamide (NMF). In oxygen atmosphere, WO_3electrode produces cathodic photocurrent which is attributed to the reduction of O_2 and anodic photocurrent is due to oxidation of NMF in the presence of N_2. A suitable mechanism is proposed for the electrode reactions.*

Keywords--- *PEC CELL, WO3, NMF, PHOTOVOLTAGE, PHOTOCURRENT*

I INTRODUCTION

Using semi conductor materials like ZnO, TiO_2, WO_3 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. **WO_3** is an n-type semi conductor with a band gap of 2.7eV. This corresponds to utilization of 11.8% solar energy. **WO_3** is reported (1) as a stable semi conductor for electrolysis of water in the presence of light. Photo catalytic activity of WO_3 is also reported (2).

In the present study **WO_3** is used as a photo electrode in a PEC cell consisting of NMF Aqueous solution as electrolyte. Photo voltages and photo currents are measured. **WO_3** in the powder state is used as photo catalyst and the products are identified.

II EXPERIMENTAL ANALYSIS

PEC cell is constructed using polycrystalline**WO_3** paste. A thin layer of **WO_3** is deposited on a platinumfoil and used as photo electrode. A platinum foilis used as counter electrode. A 1500W halogen lamp is used as light source. Electrolyte solution is a mixture of 0.1MKCl and 0.1MNMF.

WO_3,Pt/0.1 M NMF//0.1 M KCl/Pt
0.1 M KCl

III 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 N_2 than in O_2. PEC cell produces a negative photo voltage and cathodic current in the presence of visible light and O_2. In the presence of N_2 a positive voltage is developed and

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anodic current is noted (table.1). If N_2 atmosphere is not maintained properly, the adsorbed O_2 on **WO_3** electrode surface initially produces cathodic current and then anodic current as shown in (Fig.1 & 2).

Table1-Effect OfGaseoius 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 (mV)	Short circuit (μA)	Nature of Photo current
WO3 Electrode	Counter Electrode			
O2	O2	-160	4.1	Cathodic
O2	N2	-150	3.9	Cathodic
N2	O2	+55	1.5	Anodic
N2	N2	+53	1.1	Anodic

Photo voltage in O_2 reaches a limiting value within 15 minutes. It takes longer times,150 minutes in N_2. When the light is switched off, the photo voltage of the cell in O_2 decays fast while in N_2 the decay is slow (Fig. 1).

The cathodic photocurrent in O_2 increases steeply on illumination. It reaches a maximum value, then decreases fast and attain a constant value (Fig.2) when the light is switched off, rapid decay of photo current is observed in both the atmospheres.

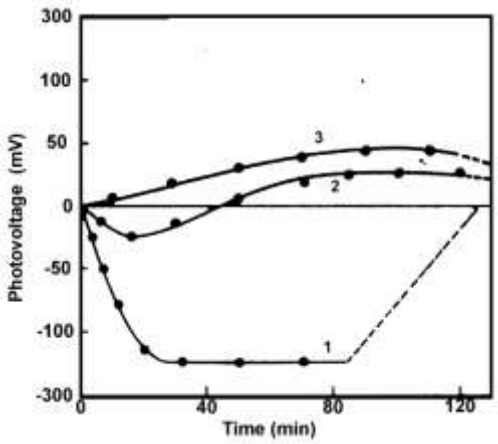


Fig.1-Variation of Photovoltage with time

- Oxygen Atmosphere
- Nitrogen Atmosphere (Bubbled for 60 minutes)
- Nitrogen Atmosphere (Bubbled for 120 Minutes)
- …….Light off

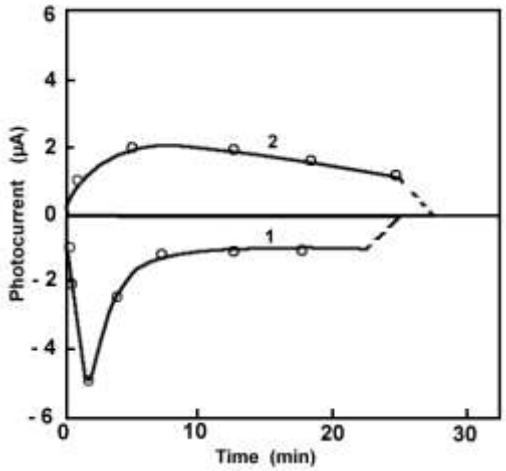


Fig2- Variation of Photocurrent with time

- Oxygen Atmosphere
- Nitrogen Atmosphere
- …….Light off

Effect of intensity of light on photo voltage in O_2 atmosphere and 0.1MKCl 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 420 nm, which corresponds to the band gap of WO_3 (2.7 eV).

The plot of photovoltageverses log of light intensity is linear (Fig 3) which shows that **WO_3** 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 O_2 is replaced by N_2 gas only anodic photo current is generated. Hence, cathodic photo current is due to reduction of O_2 to O_2^{--} Many Authors (4-7) observed similar effects on semi conductors. The super oxide IonO_2^- is a good nucleophile and can react with carboxyl compounds (9). The O_2 reacts with N-methyl formamide to give CO_2 and $CH_3.NH_2$. CO_2 is identified at the electrode. However, CO_2 is not identified in the presence of N_2.

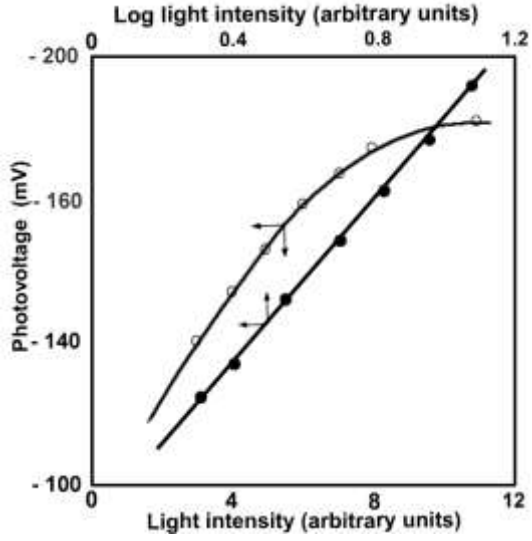


Fig3-Effect of intensity of light on photovoltage in oxygen atmosphere

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 O_2 to give O_2^- 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 maybe due to poor electron hole separation and the oxidation of O_2^{--}radical by valence band holes (reaction 3). Detection of H_2O_2 provides additional evidence for the formation of O_2^{--}(8).

The other products, CO_2 and $CH_3.NH_2$ are formed only in the presence of oxygen and under illumination. Hence the $O_2^{--}$is expected to react with DMF to give CO_2 and $CH_3.NH_2$ as shown. Protonation of NMF (reaction 6) is well known in acidic medium and this facilitates O_2^{--} attack on the carbonyl carbon of the NMF.

The anodic nature of photocurrent in nitrogen

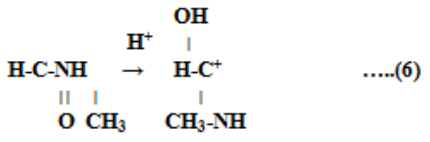
$$WO_3 \xrightarrow{h\chi} WO_3^{(+)} + e^- \quad \text{....(1)}$$

$$e^- + O_{2\,(ads)} \rightarrow O_{2\,(ads)}^- \quad \text{... (2)}$$

$$O_{2\,(ads)}^- + WO_3^{(+)} \rightarrow O_2 + WO_3 \quad \text{...(3)}$$

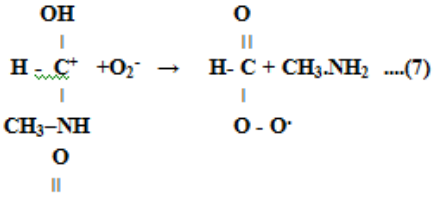
$$O_{2\,(ads)}^- + H_{(ads)}^+ \rightarrow HO_2^{\cdot} \quad \text{...(4)}$$

$$2HO_{2\,(ads)}^{\cdot} \rightarrow H_2O_2 + O_2 \quad \text{....(5)}$$



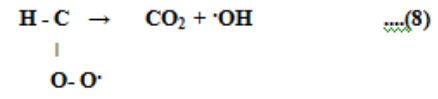
$$\text{H-C-NH} \xrightarrow{H^+} \text{H-C}^+ \quad \text{.....(6)}$$

(O, CH_3 on the left; OH, CH_3-NH on the right)



$$\text{H-C}^+ + O_2^- \rightarrow \text{H-C} + CH_3.NH_2 \quad \text{....(7)}$$

(CH_3–NH; O; O - O·)



$$\text{H-C} \rightarrow CO_2 + {\cdot}OH \quad \text{....(8)}$$

(O- O·)

$$2{\cdot}OH \rightarrow H_2O_2 \quad \text{....(9)}$$

$$WO_3^+ + OH^- \rightarrow WO_3 + {\cdot}OH \quad \text{..... (10)}$$

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.

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It has not been possible to completely eliminate either oxidation or reduction at the electrode in a particular gaseous atmosphere. Bothreations 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 formamide by valence band holes during illumination. 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).

IV 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 WO_3 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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