

Photoelectric Effects at Semiconductor Electrodes*

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Useful electrical work can be derived from photoelectric cells containing zinc oxide electrodes in contact with oxygen-free aqueous solutions containing organic compounds, or from irradiated cadmium sulfide electrodes. Study of these cells has shown that, with electron acceptors at the dark electrode, continuous current results from photolysis of the semiconductor electrode material. Steady photovoltages of 1.8 volt, open circuit, can be maintained over long periods of illumination; steady photocurrents of 1.5 ma can be delivered through 100 ohm external resistance. Zinc oxide electrodes are sensitive to the entire ultraviolet region of the spectrum. The actual operating photovoltages and/or photocurrents obtained depend on: (1) the presence of an oxidizable substrate at the irradiated zinc oxide surface, and (2) the nature and concentration of the electron acceptor at the dark electrode, as well as on the light intensity and the external load. Factors which promote the creation of positive holes in zinc oxide, such as doping with copper or silver, favor rapid response to the light and reproducible accumulation of optimum photoelectric effects. Many substances which are efficient electron acceptors at the dark electrode can be re-oxidized by atmospheric oxygen and are thus reversible. Reactions occurring at the irradiated zinc oxide or cadmium sulfide electrodes are not reversible.

Formamide and alcohols are suitable substrates for oxidation at the irradiated zinc oxide electrode. At irradiated cadmium sulfide electrodes organic oxidizable materials have no effect; the sulfide itself undergoes photo-oxidation. Ceric ions, in acid solution at the dark, reference, platinum electrode, give the highest photovoltages and photocurrents so far sustained.

INTRODUCTION

The knowledge that a photovoltaic effect can be produced in an electrical cell containing an irradiated zinc oxide electrode is not new (1). Many years ago Baur (2, 3) proposed an explanation of the production of hydrogen peroxide in irradiated zinc oxide suspensions based on an electrochemical cell model involving oxygen. Vesalovskii (4) reported a potential of

—0.6 V for Zn, ZnO (anodically polarized in 0.1 N NaOH) vs. Ag, Ag₂O electrode. He found a photocurrent proportional to the light intensity and a quantum yield of 0.5.

Reported quantum yields for photochemical processes at catalytic zinc oxide surfaces (5-7) are also of the order of 0.5 to 1.0. In view of the extensive data now available on the nature of oxygen effects at zinc oxide surfaces (8, 9) and of the role of various organic substances, especially amides (10), on the reversible formation and decomposition of hydrogen peroxide on irradiated zinc oxide, it seemed an opportune time to reinvestigate some of the photoelectric effects with more careful attention to the role of oxygen and of organic additives in the operating character-

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istics of cells containing zinc oxide electrodes.

Other substances such as zinc sulfide and cadmium sulfide have been extensively studied as photoconductive materials, and are also reported to give photovoltaic effects in aqueous systems (11). Since these sulfides are known to be extensively oxidized in contact with oxygen and light (12) it seemed advisable to investigate photoelectric effects on these semiconductors in some detail also.

In the following sections data are presented on the operation of electrochemical cells with zinc oxide electrodes under a variety of external conditions such as irradiation, atmospheres of various gases, varying external load conditions, and cell design. Several studies have also been made of effects of varying electrolyte concentrations and the nature and pretreatment of the semiconductor.

EXPERIMENTAL METHODS

The light source used in these experiments was a Hanovia H-4 high-pressure mercury arc lamp surrounded by a 2-mm Pyrex shield or envelope. In addition, a piece of heat-absorbing glass, 6 mm in thickness, supplied through the courtesy of American Optical Co., was introduced into the light path. The electrochemical cell itself was made of Pyrex 1 mm in thickness. The net effect was to isolate the 366 $m\mu$ mercury line as the only effective wavelength in the photoelectric processes, since the heat glass absorbs all radiation below 350 $m\mu$ and zinc oxide does not absorb above 380 $m\mu$. Light intensity measurements were recorded using a calibrated Eppley thermopile, having a 1-mm Pyrex window (which corresponds to the 1-mm Pyrex of the electrochemical cell) and using a Hanovia SC 5022 filter, transmission 65% to isolate the 366 $m\mu$ line. A Varian, G-14, 1 mV potentiometric recorder was used to measure the output of the thermopile. A Bausch & Lomb VOM5 recorder was used to measure the open-circuit emf of the cell and also to measure the current under load, with or without added resistance in the circuit. While meas-

uring the current with the VOM5 a separate EICO vacuum tube voltmeter was used for simultaneous voltage measurements. For extended operating periods when the cell was kept running for time-output studies, the output was measured on an Esterline-Angus recording galvanometer with a full-scale deflection of 1 ma, and a modified internal resistance of approximately 2000 ohms. Measurements made on this instrument are starred and annotated in the tables.

Zinc oxide or cadmium sulfide test electrodes were prepared by applying a paste to a cylindrical platinum gauze electrode of the usual type used for electrodeposition of metals in quantitative analysis. In the case of zinc oxide subsequent heating of the electrode for about 30 min at 300–350°C improves adherence and photoelectric response. Cadmium sulfide gives best performance when doped with copper and prepared according to the directions of Sheehan (13). Doped zinc sulfide (Cu) was prepared in an analogous manner.

Half-cells were designed to permit passage of gases over the electrode surface. The sidearms of the half-cells were filled with agar saturated with potassium chloride and connected through a reservoir of saturated potassium chloride. Potassium chloride is used as the supporting electrolyte unless special buffers are designated. The agar salt bridge is the most troublesome and least reproducible element in the cell circuit. Substitution of some type of porous membrane for the agar bridge would prolong the useful life of the cell.

All chemicals used were certified reagent grade. Attempts have been made to anodize zinc and use the oxide-coated metal as the illuminated electrode as Vesalovskii (4) apparently did, but the anodizing process has not been satisfactory. Reduction of ceric to cerous ion was followed by titration of ceric ion remaining at a given time with standard ferrous ammonium sulfate solution. Formamide forms hydroxamic acid with alkaline hydroxylamine. The hydroxamic acid produces with ferric chloride a red complex which can be used for colorimetric estimation of formamide. Ace-

tone and isopropyl alcohol were separated and estimated quantitatively by gas chromatography. The F & M Model 609 flame ionization gas chromatograph was used isothermally at 35°C with a 2-ft Carbowax 20 M column. In this method water does not interfere with the determinations.

The usual zinc oxide was Kadox 25, specific area approximately 10 m²/g, supplied by the New Jersey Zinc Co. They also provided the samples doped with silver, copper, and aluminum, indicated respectively as PZ-729R, PZ-267, and PZ-2020.

RESULTS

Preliminary Investigation of Factors Affecting Photoelectric Effects

For the initial investigation of effects of oxygen and/or illumination (366 m μ) the following cell was set up:

Pt, ZnO; 0.1 N KCl || 0.1 N KCl; ZnO, Pt
(test electrode—light) (reference, or dark, electrode)

Initially the two half-cells were identical and there was no measurable current or emf with both electrodes dark. Table 1

TABLE 1
EFFECTS OF OXYGEN, NITROGEN, AND LIGHT
AT ZINC OXIDE ELECTRODES, 0.1M KCl

Test electrode	Reference electrode	Emf (volts)	Current ^a (ma)
Dark N ₂	Dark N ₂	—	—
Dark O ₂	Dark O ₂	—	—
Dark N ₂	Dark O ₂	0.11	— (0.008)
Irrd. N ₂	Dark N ₂	0.70	0.05
Irrd. N ₂	Dark O ₂	0.75	0.21
Irrd. O ₂	Dark N ₂	0.14	—
Irrd. N ₂	Dark, bare Pt, N ₂	0.70	0.05
Irrd. N ₂	Dark, bare Pt, O ₂	0.82	0.21
Dark N ₂	Dark, bare Pt, O ₂	0.13	— (0.005)

^a 2000 ohm resistance.

shows effects of light and atmosphere at the two electrodes, and the effect of substituting a bare platinum electrode for ZnO, Pt as the reference electrode.

When zinc sulfide is substituted for zinc oxide at the test electrode the dark emf produced is about 0.3 V, and no appreciable

change takes place on irradiation. Furthermore zinc sulfide shows poor adhesive qualities to platinum when the zinc sulfide electrode is prepared in a manner similar to zinc oxide. Reagent cadmium sulfide however exhibits good adhesive properties and good photovoltaic effects. Cadmium sulfide, as will be seen below, gives more rapid response and improved photocurrents in these cells when doped with copper.

In all cases oxygen acts as a strong electron sink when present at an *n*-type photoelectrode. Negligible currents and potential differences are realized unless oxygen is removed from the test cell. It can be effectively removed by bubbling nitrogen through the cell until it reaches a maximum steady voltage. Since stirring interferes with exchange of electrons between the electrolyte and the semiconductor the cells operate best if left operating in an inert atmosphere. The process can be seen (from subsequent data) to be surface-controlled and not diffusion-controlled as long as oxidizable substrates are present at concentrations of about 0.1 M or higher. It may be diffusion-controlled under some conditions.

Effects of Adding Oxidizing and Reducing Substances to the Electrolyte

From the data above it is evident that oxygen at the zinc oxide electrode opposes the development of a potential difference, both in the dark and on irradiation. If oxygen is removed from the environment of the zinc oxide test electrode a potential difference develops even in the dark and increases rapidly on irradiation. Very little current is obtained, however, unless oxygen is present at the reference electrode. Since the concentration of oxygen dissolved in potassium chloride is very limited at atmospheric pressure, the idea immediately presented itself of substituting some other oxidant for oxygen. *p*-Benzoquinone is a good oxidant with about the same oxidation potential as oxygen, and was therefore a logical first choice. Quinone seems to be capable of playing the same role as oxygen in functioning as an electron acceptor at the dark, or reference electrode. The pH

has little effect on the photo-emf produced, but does influence the rate of charging the cell on irradiation (1). On drawing current from these cells there is a steady drop in output. Since quinone is soluble to the extent of only about 0.02 *M*, a search was made for other electron acceptors.

It was considered that if, as previous publications from this laboratory indicate (5, 7, 10, 14, 15) zinc oxide is a true catalyst for photo-oxidation of organic substances, it should be possible to provide an electron donor at the irradiated zinc oxide test electrode and thus carry out the oxidation process in an electrochemical cell. Two organic substances about whose reactions at zinc oxide surfaces considerable data had already been accumulated, were isopropyl alcohol (7) and formamide (10, 15). It was decided to investigate these additives as possible electron donors in the cell. Both substances function satisfactorily in an oxygen-free atmosphere in maintaining a steady photo-output from an irradiated zinc oxide electrode.

Using formamide at the test electrode a number, of other oxidizing substances have been tested in place of quinone and oxygen at the dark, or reference electrode with results that show a positive correlation between the photo-emf and the oxidizing potential of the oxidizing agent. The results are shown in Table 2. Ceric ion gives the highest emf and photocurrent. It is evident that dark emf values are directly related to the oxidation potential of the electron

acceptor. Light uniformly produces an increase of 0.6–0.7 V. Ceric, permanganate, and dichromate ions all require acid conditions for reduction. A variety of organic substances tested as electron donors at the zinc oxide electrode gave the results listed in Table 3.

TABLE 3
EFFECTS OF VARIOUS OXIDIZABLE SUBSTANCES
AT THE TEST ELECTRODE—ZnO—Pt^a

Oxidizable substance in the test cell (in 0.1 <i>M</i> KCl)	Dark emf (volts)	Irradiation	
		Emf (volts)	Current ^b (ma)
Methanol, 4.5 <i>M</i>	0.90	1.5	0.48
Ethanol, 4.5 <i>M</i>	0.84	1.4	0.48
Isopropanol, 0.1 <i>M</i>	1.0	1.7	0.65
Pyridine, 0.1 <i>M</i>	1.0	1.6	0.50
Formamide, 0.1 <i>M</i>	1.0	1.8	0.65
<i>N</i> -Methyl Formamide, 0.1 <i>M</i>	1.0	1.8	0.70
Acetamide, 0.1 <i>M</i>	1.0	1.8	0.50
Thioacetamide, 0.1 <i>M</i>	1.0	1.8	0.50
Urea, 0.1 <i>M</i>	1.1	1.3	0.30

^a Reference electrode: 0.1 *M* ceric sulfate-Pt.

^b 2000 ohm resistance.

A few experiments have also been conducted to investigate the possibility of using hydrogen as an electron donor at the irradiated zinc oxide electrode in these cells. It appears that hydrogen flowing over the zinc oxide surface causes a gradual increase in both the dark emf and the dark current of these cells, approaching after a few hours the maximum photo-emf of the irradiated

TABLE 2
EFFECTS OF VARIOUS REDUCIBLE SUBSTANCES AT THE REFERENCE ELECTRODE (Pt)
Test cell: ZnO—Pt. 0.1 *M* formamide in 0.1 *M* potassium chloride

Reducible substance (conc.)	St. red-ox. potential (volts)	Dark emf (volts)	Irradiation	
			Emf (volts)	Current ^a (ma)
Oxygen (sat'd. sol'n.)	0.68	0.20	0.90	0.21
Anthraquinone (sat'd. sol'n.)	0.15	—	0.32	0.05
1-2 N-Q (sat'd. sol'n.)	0.56	0.0	0.82	0.19
Paraquinone 0.02 <i>M</i> (sat'd. sol'n.)	0.70	0.20	0.95	0.23
Ferric chloride 0.1 <i>M</i>	0.77	0.64	1.3	0.35
Ceric sulphate 0.1 <i>M</i> (1 <i>M</i> H ⁺)	1.6	1.1	1.8	0.60
Potassium dichromate, 0.1 <i>M</i> (1 <i>M</i> H ⁺)	1.1	0.75	1.3	0.28
Potassium permanganate, 0.1 <i>M</i> (1 <i>M</i> H ⁺)	1.5	1.0	1.7	0.42

^a 2000 ohm resistance.

electrodes in contact with formamide. Dark current also increases in the presence of hydrogen. Irradiation serves only to increase the rate of accumulation of potential difference and current, but does not affect the magnitude. These effects are undergoing further study.

Experiments with Doped Electrodes of Zinc Oxide and Cadmium Sulfide

It is well known that the conductivity properties of zinc oxide are greatly modified by doping with silver, copper, or lithium to make the product a more positive (or a poorer electron excess) semiconductor on the one hand, or with aluminum or gallium to increase conductivity on the other hand. We had originally thought that, since the internal resistance of the cell is high due partly to grain boundaries between the zinc oxide and the platinum support, the current might be increased by using doped zinc oxides which were known to be better conductors. Some electrodes were specially prepared and used as test electrodes in cells containing 0.1 M formamide, 0.1 N potassium chloride at the test electrode, and Pt; Ce⁺⁺, 1 N H₂SO₄ at the reference electrode. Surprisingly there was very little effect on the photocurrents produced,

and very little difference among the observed photo-emf values at maximum. There was a considerable difference in the time required to reach the maximum photo-emf. The results are summarized in Table 4.

Table 4 also shows the effect of doping cadmium sulfide with copper, and of mixing zinc oxide and cadmium sulfide in order to try to sensitize the electrode to longer wavelengths. Formamide does nothing to increase the output in the case of the mixed electrode, or of any of the cadmium sulfide electrodes. In agreement with Williams we find cadmium ion and sulfur to be the products formed in the case of the cadmium sulfide electrodes. Fastest and best response of electrodes to irradiation occurs with silver or copper doping, i.e. with increase in *p*-type character, or ability to form positive holes.

Reactions Occurring at the Electrode Surfaces

The foregoing data suggest that an irradiated zinc oxide electrode can function as an element of a fuel cell, effecting an exchange of electrons between an organic oxidizable material and an oxidant such as oxygen, quinone, or ceric salts. Oxygen has the disadvantage of low concentration as the electron acceptor unless subjected to high pressure. Quinone has a limited solubility in water, but the concentration can be increased in solvents with partial alcohol content. Characteristics of cells containing *p*-benzoquinone are influenced by pH. In a chloroacetate buffer around pH 3, the response of emf and current to irradiation is very rapid. If the quinone is used as an electron acceptor around pH 9, the response is much more sluggish (1). Once the maximum photo-emf has been attained, it is dissipated more slowly also when irradiation stops. For some purposes this might be an advantage.

The formamide or alcohol concentration governs the steady state photocurrent output. Time studies of the cell: Pt, ZnO (N₂); formamide, 0.1 M KCl || sat'd quinone, 10⁻³ M H⁺; Pt are recorded in Fig. 1. It is evident that the duration of steady

TABLE 4
EFFECTS OF PHOTOCONDUCTIVE MATERIAL AT THE TEST ELECTRODE (0.1 M Ce⁺⁺, 1 M H⁺; Pt; REF. ELECTRODE)

Test electrode (0.1 M formamide, 0.1 M KCl)	Dark emf (volts)	Irradiation		Time to reach max. emf (min)
		Emf (volts)	Current ^a (ma)	
ZnO spect. grade	1.1	1.8	0.60	10
ZnO (Ag)	1.2	1.8	0.50	1
ZnO (Al)	1.3	1.4	0.45	30
ZnO + CdS (4:1)	1.2	1.8	0.50	—
ZnO, photoconduc- tive (New Jersey Zinc Co.)	0.90	1.6	0.78	—
CdS (reagent grade)	1.2	1.5	0.35	—
CdS (Cu)	1.2	1.85	0.75	—
ZnS (Cu)	0.65	0.88	0.03	—
CdO (reagent grade)	1.0	—	—	—
CdO (Cu)	1.1	—	—	—

^a 2000 ohm resistance.

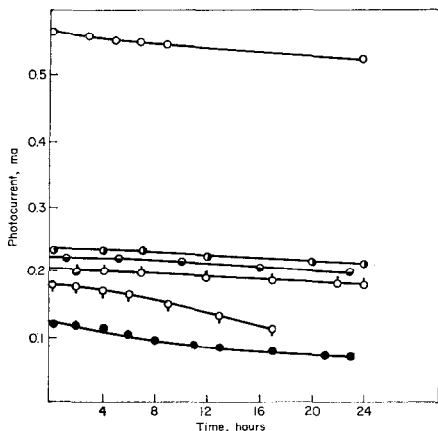


FIG. 1. Variation in photocurrent with concentration of formamide; external load 2000 ohms. Cell:

Pt, ZnO; 0.1 N KCl, formamide||
sat'd *p*-quinone, pH 3; Pt

Formamide concentration: (●) 100%; (○) 1 M;
(◻, ◻) 0.1 M; (◊) 0.01 M; (◇) 0.001 M. In
the highest curve (○), Ce⁴⁺, 1 M H⁺ substituted
for quinone.

photo-emf and photocurrent production is dependent on the concentration of formamide, and that the optimum concentration is about 1 M. This concentration is like-

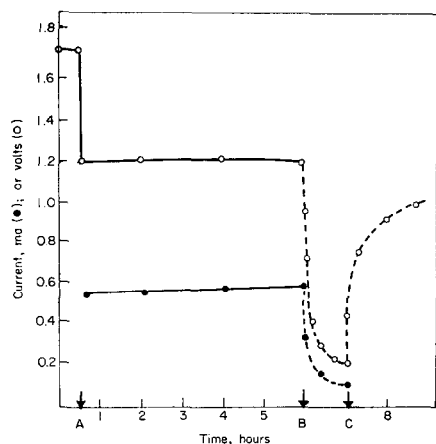


FIG. 2. Current (●)-voltage (○) output of the cell:

Pt, ZnO; 0.1 M formamide, 0.1 N KCl||
0.1 M Ce⁴⁺, 1 M H⁺; Pt;
A: commencement of drawing current; B: end of
irradiation; C: end of drawing current.

wise optimum for isopropyl alcohol. It is also evident from Fig. 2 that the current falls rapidly if drawn after irradiation is discontinued. The emf however regains the usual dark value of about 1.0–1.1 V if no current is drawn in the dark.

Since ceric ion produces the highest steady state photo-emf and hence photocurrent, cells containing ceric ion as the electron acceptor received special study. Table 5 shows the relation between equiva-

TABLE 5
RELATION OF EQUIVALENTS OF ELECTRICITY
DRAWN TO EQUIVALENTS OF CERIC ION
REDUCED, AND ZINC ION ACCUMULATED
IN CELLS CONTAINING 0.1 M
ISOPROPYL ALCOHOL

Faradays drawn ($\times 10^3$)	Ceric ion reduced (milliequivalents)	Zinc ion accumulated (milliequivalents)
0.71	1.07	0.64
0.72	1.09	0.54
0.08	0.07	0.06
0.09	0.09	0.08
0.62 ^a	0.51 ^a	0.54 ^a

^a This experiment 0.1 M formamide was used in place of isopropyl alcohol.

lents of ceric ion reduced and current drawn for cells containing 0.1 M formamide or 0.1 M isopropyl alcohol in the irradiated zinc oxide half-cell and ceric ion in approximately 6 M sulfuric acid in the dark half-cell. It is seen that the amount of ceric ion reduced corresponds closely to the electrochemical equivalent of the current. It is also found that the number of equivalents of zinc ion found in solution in the zinc oxide half-cell increases in proportion to time of operation or current drawn. The solubility of Kadox-25 in 0.1 N potassium chloride is otherwise about 1×10^{-4} M.

Figure 3 shows the variation in zinc ion concentration with time of operation of the cells. In the case of 0.1 M formamide as the oxidizable organic substrate there is an initial lag in the release of zinc ions, which appeared to indicate after short term runs that the zinc oxide electrode was acting as a true photocatalyst. A peculiar observation is that the apparent number of equivalents

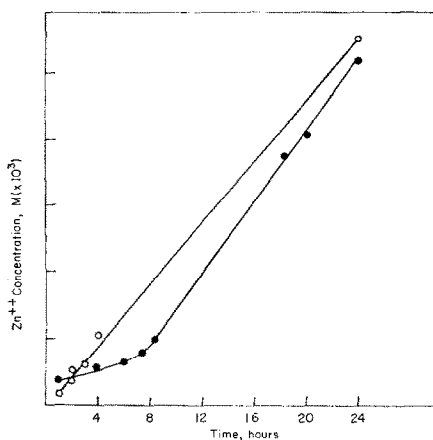


FIG. 3. Accumulation of zinc ion in zinc oxide half-cells in relation to current drawn during time of operation of cell:

formamide
 Pt, ZnO; 0.1 N KCl, or , 0.1 M ||
 isopropyl alcohol
 0.1 M Ce⁺⁺, 1 M H⁺; Pt;

(●) cells containing 0.1 M formamide; (○) cells containing 0.1 M isopropyl alcohol.

of formamide consumed in the early stages of operation of these cells is several times that expected from the ceric ion reduced. There is a possibility that formamide is isomerizing at the zinc oxide surface before being oxidized (16). The color test employed, the most sensitive we have found so far, is not particularly stable nor easy to reproduce. There is certainly still some question as to the accuracy of these measurements of formamide concentration, but even allowing a considerable margin of error, there is something happening to formamide which is not being detected.

The problem becomes more acute in that the cell certainly does not behave as if it were depleted of formamide in a few hours. Some of these cells have run 48 hr with only a slight drop in efficiency.

We have studied the oxidation of formamide in irradiated zinc oxide suspensions, and we have found cyanate ion accumulating on the zinc oxide surface during the oxidation (17). Cyanate ions are also found adsorbed on zinc oxide removed from electrodes that have been functioning in these

cells. Oxygen is not necessary for the formation of cyanate from formamide, which needs only to lose two electrons and two hydrogen ions in the process. There is no certainty that cyanate is the final oxidation product in these reactions, but the difficulty in analyzing for possible nonvolatile oxidation products of formamide in dilute aqueous solutions makes an exhaustive study of the products prohibitive. A series of tests were carried out to determine whether added cyanate would decrease the photoelectric output of cells containing formamide. The results are presented in Fig. 4.

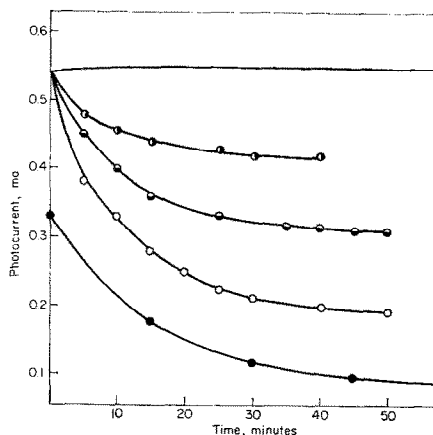


FIG. 4. Effect of addition of KCNO (possible oxidation product of formamide) to the photocell containing ZnO, formamide, 0.1 M, and ceric bisulfate, 0.1 M. Concentrations of cyanate: 0.00 M (—); 0.05 M (●); 0.1 M (◐); 0.1 M, no formamide (○); 0.0 M, no irradiation (●).

It can be seen that if half the formamide (as suggested by color tests) had really been converted to cyanate in 6 hr, there would have been a larger drop in photocurrent. The cell actually operates with a steady output as indicated by the solid lines in Fig. 1. Furthermore by infrared analysis (17) 0.05 M cyanate shows much stronger adsorption on zinc oxide than that which we record as accumulated on the zinc oxide electrode after several hours. It would appear that the cyanate concentration in the electrolyte even after 6 hr is less than 0.001 M.

The difficulties in accounting for the

oxidation (or hydrolysis or isomerization) of formamide under these conditions have initiated a search for an electron donor whose products could be quantitatively accounted for. The cells operating on isopropyl alcohol, with acetone as the product, show an even closer equivalence between current drawn, reduction of ceric ion, and accumulation of acetone and zinc ion. At a concentration of about 0.25 *M*, acetone produces a 15% reduction of the initial output of the cell.

In cells operating with irradiated cadmium sulfide electrodes, the sulfide ion of the semiconductor itself is evidently the oxidizable substrate, the products being sulfur and cadmium ions. Cadmium ion accumulates at a rate of 2.6×10^{-3} moles/liter hr, while ceric ion is reduced at a rate of 5.7×10^{-3} moles/liter hr; thus the rate of reduction of cerium is almost completely compensated by oxidation of cadmium sulfide. Even in experiments with mixed electrodes containing both zinc oxide and cadmium sulfide (cf. Table 4) it is the cadmium ion which accumulates in the electrolyte of the test cell, not the zinc.

Calculation of Energy Transfer and Quantum Efficiency

It has been stated previously that the operating values of photocurrent and photo-emf depend in part on the load in series. The cells have a high internal resistance and the output is dependent on surface reactions. Too rapid discharge of current drains the cell faster than electrons can be released. Data presented in Table 6 show that the cell containing isopropyl alcohol functions with optimum current and voltage output with about 1000 ohm external load.

Table 7 shows the relationship between light energy input and electrical energy output for a zinc oxide cell operating at 366 $m\mu$. The emf as measured by the vacuum tube voltmeter remains constant over a wide range of light intensities. The current falls off rapidly with decreasing light intensity and tends to a light saturation at high light intensities. The result is that there is an optimum light intensity region for maximum efficiency of the cell with an

TABLE 6
VARIATION OF EMF AND CURRENT WITH LOAD
IN CELL Pt. ZnO; 0.1 *M* ISOPROPANOL,
0.1 *M* KCl || 0.1 *M* Ce⁴⁺, 1 *M* H⁺; Pt

Resistance (ohms)	Emf (volts) under load	Current (ma) 1000 ohm load	Emf \times current
200	0.28	1.4	0.392
400	0.48	1.2	0.576
600	0.65	1.0	0.650
800	0.74	1.0	0.740
1,000	0.85	0.90	0.765
1,200	0.92	0.81	0.745
1,400	0.98	0.74	0.725
1,600	1.02	0.68	0.694
1,800	1.06	0.63	0.668
2,000	1.10	0.59	0.649
3,000	1.40	0.43	0.602
10,000	1.46	0.15	0.291

external load of 1000 ohms. It must be remembered that whereas these measurements were made at 366 $m\mu$, zinc oxide actually absorbs throughout the ultraviolet region of the spectrum, and although this would increase the range of useful actinic light, there is no data on the efficiency at other wavelengths; 366 $m\mu$ is close to the threshold absorption value of 380 $m\mu$ for zinc oxide in the near ultraviolet. With small loads of a few ohms these cells will deliver 3 ma continuously for periods of time depending on the concentration of the organic additive.

If the only reaction were photolysis of zinc oxide there would be a large positive free energy change in this reaction. However the concomitant and apparently necessary oxidation of isopropyl alcohol, for example, a little more than compensates. Thus there appears to be no energy storage in the system, and an over-all conversion of about 20% of the ultraviolet energy to electrical energy.

DISCUSSION

In agreement with Williams' investigation of the Becquerel photovoltaic effect in cadmium sulfide, we find that photolysis accompanies the production of photocurrent, resulting in formation of cadmium ion and sulfur. The increase in emf or irradiation is 0.6–0.7 V, also in agreement with his

TABLE 7
RELATION OF LIGHT ENERGY INPUT TO ELECTRICAL ENERGY OUTPUT

(1) Light intensity on electrode surface (mW)	(2) Emf (VTVM)	Operating under 1000 ohm load		(5) Product (3) × (4) Electrical energy (mW)	(6) Efficiency (5) / (1) Light energy Electrical energy
		(3) Emf (volts)	(4) Current (ma)		
18.9	1.70	0.90	0.95	0.86	0.05
10.7	1.70	0.88	0.93	0.82	0.08
2.7	1.70	0.72	0.75	0.54	0.20
1.2	1.65	0.47	0.50	0.24	0.20
0.70	1.60	0.33	0.33	0.11	0.16
0.43	1.60	0.20	0.22	0.04	0.10

findings. By operating the cadmium sulfide half-cell vs. a half-cell containing acidified ceric ions, the photo-emf reaches 1.85 V, or 0.75 V above the dark voltage of 1.1 V for the cell. The interesting observation in these experiments is that the higher operating emf allows a much higher photocurrent to be drawn from the cell under reasonably high operating loads.

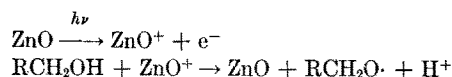
When a substantial per cent of ceric ion has been reduced to cerous, ceric ion can be regenerated by running the ceric half-cell against a catalytic oxygen electrode in the dark (e.g., Pt-black, O₂, dil. H⁺). Since the concentration of oxygen maintained by drawing air over the platinum-black electrode is low at atmospheric pressure, and the potential difference between oxygen and ceric ion is small, the regeneration process is slow compared to the discharge process.

In the absence of oxygen the zinc oxide photocell gives comparable values of photo-emf and photocurrent, but can maintain them only on addition of organic substances oxidizable at the irradiated zinc oxide electrode. Doping of zinc oxide influences chiefly the rate of attaining the maximum operating photo-emf, to which the photocurrent is proportional in most cases.

Early experiments using formamide as the additive seemed to indicate that the zinc oxide electrode was a true catalytic electrode, bringing about oxidation of organic substances in the absence of oxygen. During short-term operation of a zinc oxide photocell containing formamide there is very little accumulation of zinc ion in solu-

tion, as seen in Fig. 3. Over long operating periods however, zinc ion does accumulate. On substituting isopropyl alcohol as the organic additive, the zinc ion accumulation is almost linear. Oxidation of the organic additive therefore seems to be accompanied by photolysis of zinc oxide. The function of the organic additive may be either:

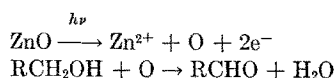
(1) direct transfer of electrons to the irradiated zinc oxide,



followed by



or (2) removal of oxygen, thus preventing recombination,



In either case the reaction involving the organic additive at the zinc oxide electrode is irreversible, and the electrical work is performed at the expense of the oxidation of the organic material. Zinc ion can be reprecipitated as the hydroxide or carbonate and roasted to form zinc oxide again. The low value of the photo-emf reported for zinc oxide by Williams was undoubtedly due to the presence of oxygen at the surface of the zinc oxide electrode.

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