MASTER

HYDROGEN AND METHANE SYNTHESSES
THROUGH RADIATION CATALYSIS

MASTER

Progress Report
for Period June 1, 1977 - August 31, 1978

J. G. Morse
COLORADO ENERGY RESEARCH INSTITUTE
Golden, Colorado 80401

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

September 1978

Prepared for

THE U. S. DEPARTMENT OF ENERGY

UNDER CONTRACT NO. EG-77-C-02-4258.A000

2B
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately owned rights.

ABSTRACT

Preliminary testing was performed of the concept of an electronic theory of catalysis to relate electrical properties of the catalysts to increased rates in radiation-induced reactions. The first system selected for study was the radiolysis of water as stimulated by absorption of gamma radiation, a system that has been thoroughly tested by numerous workers all in excellent agreement.

Early results indicate a significant correspondence between hydrogen gas yield and the forbidden band gap (E_g) of the catalyst substrate, when E_g approximates the energy of the hydrogen-oxygen bond in the water molecule.

Equipment to measure dielectric properties of solids has been built and calibrated, and will now be applied to pre- and post-irradiation testing of the catalysts used.

PREFACE

Under the terms of this contract, the experimental research related to catalyst definition and radiation testing was to be performed in the Physics Department at the Colorado School of Mines, Golden, and that relating to thin film preparation and electrical property measurements, pre and post-irradiation, was to be done in the Electrical Engineering Department at Colorado State University, Fort Collins. Dr. Joel DuBow, CSU, was co-investigator on the project. Both schools are involved in detailed program definition and evaluation of data collected.

TABLE OF CONTENTS

	<u>Page</u>
NOTICE	i
ABSTRACT	ii
PREFACE.	iii
LIST OF TABLES	iv
LIST OF FIGURES.	v
INTRODUCTION	1
BACKGROUND	2
EXPERIMENTAL DESIGN - RADIATION STUDIES.	6
PROCEDURE.	18
EXPERIMENTAL RESULTS	19
ANALYSIS OF DATA	19
CONCLUSIONS.	38
FUTURE WORK.	40
APPENDIX I - TABULATION OF EXPERIMENTAL DATA . . .	41
APPENDIX II - EQUIPMENT CALIBRATION.	48
BIBLIOGRAPHY	56
ACKNOWLEDGEMENTS	58

LIST OF TABLES

	<u>Page</u>
1. RADIATION CATALYSIS TESTS	20
2. AVERAGE COUNTS FOR A 300 MINUTE PERIOD.	22
3. VALUES OF n_H , ppm (H_2), G (H_2) FOR THE CATALYSTS	23

APPENDIX I

1. EXPERIMENTAL DATA	41
--------------------------------	----

APPENDIX II

1. ABSORBANCE VALUES	50
2. DOSE RATE VALUES.	50
3. CHANGE IN RADIATION DOSE WITH TIME.	50
4. RESULTS OF CALIBRATION GAS RUNS	52
5. CALIBRATION OF FLOW METER	54

LIST OF FIGURES

	<u>Page</u>
1. EXPERIMENTAL SETUP	7
2. AUTOMATION OF INTEGRATOR	9
3. DIFFERENTIAL FLOW CONTROLLER	10
4. TYPICAL H ₂ PEAK.	13
5. RADIATION VESSEL	14
6. RADIATION VESSEL SUPPORT	15
7. RUN #127 - H ₂ O + MoO ₃	24
8. RUN #121 - H ₂ O + MoO ₂	25
9. RUN #134 - H ₂ O + In ₂ O ₃	26
10. RUN #138 - H ₂ O + TiO ₂	27
11. RUN #120 - H ₂ O + TiO ₂	28
12. RUN #128 - H ₂ O + V ₂ O ₅	29
13. RUN #137 - H ₂ O + MgO	30
14. RUN #119 - H ₂ O + MgO	31
15. RUN #136 - H ₂ O + Sb ₂ O ₃	32
16. RUN #131 - H ₂ O + HfO ₂	33
17. RUN #130 - H ₂ O + SnO ₂	34
18. RUN #139 - H ₂ O	35
19. RUN #132 - H ₂ O	36
20. RUN #118 - H ₂ O	37
21. BAND GAP VERSUS H ₂ YIELD (ppm)	39

INTRODUCTION

Ionizing radiation has been shown to increase reaction rates by up to two orders of magnitude. This radiation generates electron-hole pairs through optical or radioactive stimulus. The radioactive excitation by sub-damage threshold radiation allows the continuous generation of metastable high energy carrier pairs. In this manner, energies other than the band gap may be obtained. In this investigation several surface and bulk catalyst evaluation techniques will be correlated with reaction rate data to test the concept of the electronic theory of catalysts and develop catalysts for two commercially significant processes.

"The tests of this theory have involved the measurement of the rate of some test reaction as a function of the bulk doping of the catalyst, or as a function of the band gap of the catalyst. The latter method, which is described in detail by Krylov, has been criticized, particularly on the basis that the induced surface states for a particular reaction on the various catalysts bear no simple relation to the band gap. Effects of the E_F^* on the rate may, in principle, be studied by changing E_F in one catalyst by illumination, by an external field, or by straining the catalyst sample. Unfortunately, side effects such as the creation of defects, trap centers, or dislocation and the polarization of adsorbed species in the external field make the interpretation of such experiments hazardous unless several of these techniques are employed concurrently. Apparently, this has not been done.⁽¹⁾"

* $E_F = E_g$ = forbidden band gap.

BACKGROUND

The inclusion of a solid catalyst in ionizing radiation-induced synthesis is a relatively recent innovation ⁽²⁾ in the long history of catalysis, and it necessitates further examination of the role of the solid in view of the new environment. Earlier workers in radiation catalysis observed many interesting qualitative correlations exhibiting varying degrees of conclusiveness between the surface and bulk electrical properties of the solid and its catalytic behavior. Some of the more relevant work will be noted here.

Most investigators subscribe to the adsorption of the reacting species onto the solid substrate, as an initial step prior to effecting a chemical reaction. In the radiation environment, energy from the radiant source is absorbed by this solid prior to, during and post adsorption. It is also absorbed by reactants and products. Coekelbergs et al ⁽³⁾ suggested the existence of an energy transfer mechanism for that which is absorbed by the substrate and then conveyed to the adsorbed reactant. In his review article, Krylov⁽⁴⁾ examined the relationship between catalytic activity and the width of the forbidden band gap (E_g) for solid basic oxides in the dehydrogenation of alcohols. Some were semi-conductors, others were electrical insulators, and some degree of correlation was observed. In interpreting the latter, he points out that under conditions of continuous formation and annihilation of free electrons and positive hole pairs, the system (catalyst and reactants) is not in a state of thermodynamic equilibrium. To explain this, he suggested a relationship involving the Fermi levels of the solid. More recently,

Klissurski (5) corroborated the above by relating the bond energies in metal oxides to both their E_g 's and their catalytic activity. His data include only those oxides of low E_g .

Further, Krylov (4) advanced an explanation of radiation catalysis reported in 1966, the original of which was not available. Through the recombination of free electrons with positive holes, formed during radiation absorption, photon energy is released directly to the adsorbed species. This photon energy is equivalent in magnitude to the value of E_g . If this is greater than the bond energy within the adsorbed molecule, the bond will rupture and a reaction will ensue. This explanation, if it can be verified, could establish an important criterion for catalyst selection in radiation catalysis. Because of the magnitude of required E_g 's, most of the materials of concern will be insulators.

An electronic theory of catalysis is consistent with an increasingly large body of evidence. (6) Spurred by the requirements of semiconductors, insulators and interface layers between materials have been explained with much higher degree of precision than they were prior to 1960. (7,8) Recently, a controversy has arisen concerning the nature of the barrier formed on semiconducting substrates when a conducting film is deposited upon them. (9,10) Moreover, as device performance levels have improved, and semiconducting materials other than silicon have been used, the effects of deep impurities have become increasingly important. This need for information has led to improved frequency and time dependent measurement techniques to better determine the impurity structure of solids.

These impurity structures are critical to the catalytic investigation proposed here. The carrier lifetimes, generation and recombination of barriers. Radiation affects these lifetimes by generating carriers and, if the energy of the incoming radiation exceeds a threshold energy, E_d , by generating defect centers.⁽¹¹⁾ In addition, the free carriers generated have an energy exceeding that of the band gap. For example, 0.1 MeV electrons bombarding silicon transfer 8.2 eV of energy to an electron. The result is analogous to that observed in the high field region of avalanche photodiodes. Visible light is emitted from silicon even though silicon is an indirect gap material whose energy gap is 1.1 eV.⁽¹²⁾

Verification of the electronic theory of catalysis requires prior knowledge of the electronic properties of the catalysts. These properties involve the physics of charge transfer complex formation at the surface,⁽¹³⁾ the electron affinity and work function of the semiconductor⁽¹⁴⁾ and the properties of gases such as hydrogen, chemisorbed upon the surface.⁽¹⁵⁾

The concept of reactions utilizing centers in the forbidden gap is noteworthy.⁽¹⁶⁾ Acceptor reactions are those in which the rate determining step is the transfer of an electron from the catalyst to the adsorbed particles. In donor reactions, the transfer proceeds in the opposite direction. More rigorous analyses relating to the Fermi level is displaced towards the conduction band, and donor reactions accelerate under the reverse conditions.

The above suggests an important role for dopants in catalysis. To increase the rate of an acceptor reaction, one should introduce

a dopant into a catalyst that increases its electronic conductivity. To increase the rate of a donor reaction, it is necessary to use dopants which increase the catalyst's hole concentration of conductivity. Examples of the above with semi conductors include: (a) $H_2 - D_2$ exchange on a ZnO catalyst, shown to be an acceptor reaction, was accelerated when ZnO was doped with Al_2O_3 or Ga_2O_3 (ZnO is an n-type semiconductor), (b) N_2O decomposition on NiO (p-type), as a donor reaction, was accelerated when Li_2O was used as a dopant, and decelerated when In_2O_3 was introduced into NiO.

The physics of surfaces is not well enough developed to permit a first principles description of surface properties. Both phenomenological as well as fundamental properties are required to describe the electronic and optical interactions of light, charge and films upon a given surface.⁽¹⁶⁾ A number of phenomenological techniques have been developed to elucidate impurity distributions in non-crystalline insulators, and they will be applied to determine both d.c. and a.c. conduction mechanisms of the material used in this program. Specifically, the thermally stimulated photo-and electrical conduction,⁽¹⁷⁾ along with the space charge limited current characteristics⁽¹⁸⁾ are essential for uncovering charge transfer dynamics in materials whose forbidden gaps are populated with many impurities.

The materials used in this research are generally wide gap insulators. Finely divided powders were used initially. Later, ion beam sputtered films will be used. Oxide films tend to provide

high energy gaps and higher stability with hydrogen and sulfur attack than do halide films. (19,20) Moreover, there have recently been great improvements in the quality of oxide materials available because of their application in opto-electronic devices. In addition, since the available electron energy can exceed the band-gap, a precise match of bandgap to bond-breaking energies may not be required.

In summary, the many advances in materials technology and surface characterizing make it particularly timely to investigate the electronic theory of catalysis. Emphasis, therefore, is placed on the electronic properties of the surface and the influence on these by ionizing radiation because it is believed that these may be the critical variables in radiation-induced catalysis.

EXPERIMENTAL DESIGN - IRRADIATION STUDIES

Deionized water (resistivity approximately 2 megohms) and a solid in powder form were contained in a specially designed glass vessel which was placed in a gamma radiation field. The transport gas, nitrogen, was bubbled through the water to suspend the catalyst, create a fluidized bed to maximize surface exposure to radiation, and to transport any hydrogen generated, by radiation induced catalysis, to a gas chromatograph for analysis. The experimental setup is shown in Figure 1.

Apparatus

1. Gas Chromatograph:

A Carle Analytical Gas Chromatograph Model #111, with automatic sampler, was used for the detection of hydrogen. A six foot molecular sieve 5A 45/60 column was used for the analytical column.

Figure 1 — Experimental Setup

The carrier gas was high purity dry grade nitrogen (purity of 99.995%). Nitrogen pressure of 17 psi produced a flow rate of approximately 10 cc/min. The columns and detector in the gas chromatograph were kept at a constant temperature of 40°C by a full proportional temperature controller. The carrier gas flow rate and temperature setting determines the time which the gas chromatography detects the hydrogen. Control settings were the same for all runs and were as follows:

Readout - left column

Bridge setting - thermistor

Output - 1024

Temperature - 40°C

Inlet ΔT - off

Power - on

The auto sampler part of the gas chromatograph enabled automatic sampling of the transport gas at a maximum of one hour intervals. Auto sampling of most runs was done at 30 minute intervals for a period of five minutes. Relay RY2, shown in Figure 2, contained three unused contacts which were used to automate the integrator.

2. Digital Integrator:

A digital integrator (Columbia Scientific Industries model number CSI-38) was used to determine the absolute number of hydrogen molecules. The count (C) = $\int_{T_1}^{T_2} (V_{GC} - V_{BC}) dT$ where T_1 and T_2 are the integrate on and off times respectively; V_{GS} is the chromatograph signal voltage and V_{BC} is the baseline correction voltage. The integrator, at the end of each peak, prints the count and the time of the peak. In these experiments the hydrogen peak was observed at approximately 70 seconds. The integrator was connected to

Figure 2 — Automation of Integrator

Figure 3 — Differential Flow Controller

unused relay contacts in the auto sampler of the gas chromatograph to synchronize with gas chromatograph analyses and reset after the gas chromatograph was finished (Figure 2). Control settings were constant for all runs as follows:

Recorder - 1
Peak sensitivity - 2
Power - on

3. Gamma Cell:

An Atomic Energy of Canada Limited (Model 220) ^{60}Co Well-Type Gamma Cell was used for the irradiation. The gamma cell has entry access to allow gas flow via tygon to the radiation vessel in the radiation well. The cell was located at the Veterans Administration Hospital, Denver, Colorado. The measured dose rate was 3.4×10^5 rads/hr on September 29, 1977.

4. Flow Controller:

A Whitey Micrometer Valve (#B-22R54) and Moore Flow Controller (Model SD63SUL) were used to adjust and regulate the flow of the nitrogen transport gas. The flow controller is a differential type device (see Figure 3). When the input pressure P_1 is applied to the valve and to the top of the controller's diaphragm, the diaphragm and plunger are forced down. The differential spring and downstream pressure P_2 force the diaphragm and plunger up. The differential spring produces an upward force equivalent to one produced by a constant pressure K . A pressure drop ΔP is developed across the micrometer valve due to its restriction of the flow. The controller is balanced when $P_1 = P_2 + K$, but since $\Delta P = P_1 - P_2$; $\Delta P = K = \text{constant}$, thus the flow is constant.

5. Flowmeter:

Two Fisher Porter (Model #10A2735B) Ball Type Flowmeters were

used to measure the flow rate of both nitrogen gas flows. The transport gas flow was normally set at 50cc/min and the gas chromatograph carrier gas flow at 10cc/min. It was found that the flowmeters were not linear and did not give true actual flow rates. A correction factor for the readings was necessary to adjust the flow rates to actual cc/min. (See Appendix for its calibration)

6. Chart Recorder:

An Esterline Angus 0-10 millivolt strip chart recorder in conjunction with an Omega Omni-Amp II millivolt amplifier was used to graph the output of the gas chromatograph. The recorder and amplifier were used to monitor the output during the setup and certain calibrations. A typical graph is shown in Figure 4. The recorder was run at speed of .75 inches per minute and the amplifier gain at x5.

7. Radiation Vessel:

The radiation vessels used were made from pyrex glass by R. H. Allen Company, Boulder Colorado. The vessels were cylindrical in shape 3.8 cm O.D. and a height of 16.3 cm. (Figure 5). A medium porous glass frit was located 1.5 cm. from the bottom of the vessel, with an inlet tube for nitrogen gas located below the frit. A removable ground glass cap with a 1/4 in. glass tube for gas exit, was used for access into the vessel, (for filling, emptying and cleaning). A special aluminum holder was made to support the vessel in an upright position while in the gamma cell, see Figure 6. The bottom of the vessel goes into the base support and is held upright three two inch long aluminum wires which are fastened to the base of the support. Since the aluminum base shields only the portion of the reaction vessel below the frit, no radiation

Figure 4 — Typical H₂ Peak

Figure 5 — Radiation Vessel

Figure 6 — Radiation Vessel Support

attenuation factor need be applied to the water containing catalysts. Nitrogen flowed up through the frit, bubbling through the water, suspending the powdered catalyst and exiting through the cap, transporting any gases produced by water decomposition.

8. Drierite Filter:

A 2 ft x 1 1/2 inch glass tube filled with indicating drierite #4 and #6 was used to dry the transport gas before entering the gas chromatograph. The presence of moisture reduces both performance and life of the molecular sieve column. The glass tube was filled with drierite and plugged with glass wool. Glass tubing enabled entry and exit of the gas. Indicating drierite turns from blue to pink upon absorption of moisture. The filter needed only to be changed once in three months of nearly continuous use.

9. Catalysts (Source and Purity)

(I) TiO_2

Supplier: Materials Research Corp., Orangeburg, NY
99.998% pure (-200 mesh).

Impurities:

Sn	< 30 parts per million (ppm)
Pb	< 20 ppm
Si	< 7 ppm
Mg	< 1 ppm
Ca & Ag	< 1 ppm

(II) SrTiO_3

Supplier: Materials Research Corp., Orangeburg, NY
99.5% (-200 mesh).

Impurities:

Sn	0.003%	Alkaline metals <	0.01%
Pb	0.003%	other <	0.01%
Is	0.0007%		
Mg	0.0001%		
Ca <	0.0001%		
Ag <	0.0001%		
Cl	0.002%		
NO ₃	0.01%		
So ₄	0.005%		
Ba ⁴	0.005%		

(III) Sb₂O₃Supplier: J. T. Baker Chemical Co., Phillipsburg, NJMaximum limit of Impurities:

Fe	0.01%
Cl	0.005%
SO ₃	0.01%

Insoluble residue - trace

(IV) MoO₃Supplier: J. T. Baker Chemical Co., Phillipsburg, NJAssay (MoO₃) 102.1%

Insoluble in Dilute NH ₄ OH	0.005%
Chloride (Cl)	0.002%
Nitrate (NO ₃)	0.003%
Arsenate, phosphate & silicate (SiO ₂)	< 0.001%
Sulfate (SO ₄)	< 0.02%
Ammonium (NH ₄)	0.001%
Heavy metals (Pb)	< 0.005%
Trace impurity (part per million) Phosphate (PO ₄)	< 5

(V) Nb₂O₅Supplier: Alfa Division, Ventron Corp., Danvers, MAPurity: 99.9+% pure (-325 mesh).(VI) SnO₂Supplier: Alfa Division, Ventron Corp., Danvers, MAPurity: 99.9+% pure (-20 mesh).(VII) CaOSupplier: Alfa Division, Ventron Corp., Danvers, MAPurity: 99.95%

Fluoride < 15 ppm (parts per million).

(VII) HfO₂Supplier: Alfa Division, Ventron Corp., Danvers, MA
Spectrographic grade.

The identity of all the chemicals obtained from Alfa is confirmed by x-ray diffraction and the x-ray diffraction patterns agree with the ASTM (American Society for Testing of Materials) published standards.

PROCEDURE

- (1) Integrator, recorder, and Omni-Amp were warmed up for a minimum of fifteen minutes with control settings as described in the experimental design section. Normally the gas chromatograph was left on continuously with the carrier gas flowing through it. If the gas chromatograph was shut down, it was necessary to allow it to warm up a minimum of one hour with control settings as described in the experimental design section. During this warm up period, nitrogen flowed through the gas chromatograph sample loop and sampled a minimum of every five minutes. This purged the gas chromatograph columns.
- (2) Radiation vessel was cleaned thoroughly with deionized water.
- (3) Radiation vessel was filled with 100cc deionized water and the lid was placed on the vessel.
- (4) The Gamma Cell well was raised and the vessel was placed in its support in the well. Tygon tubing, connected to the flow controller, goes in to the Gamma Cell, via entry ports, was connected to the inlet tube of the vessel. Similarly the tygon tubing going to the drierite filter was connected to the exit tube in the lid of the vessel.
- (5) The micrometer valve was open approximately one quarter of maximum. Transport gas regulator pressure was increased until (usually 50-70 psi) a reading of 50cc/min was measured by the flowmeter.
- (6) The lid was removed from the radiation vessel and the catalyst (usually .75 grams) was added. The lid was then replaced.
- (7) The micrometer valve was adjusted as necessary to bring flow rate to 50 cc/min.
- (8) The system was allowed to stabilize for fifteen minutes. Any contaminants in the system are normally swept out by the transport gas in this time. The gas chromatograph sampler was activated. If any impurities were detected by the gas chromatograph, samples were taken every five minutes until the system was clean.
- (9) The flow rate was checked and adjusted if necessary to 50cc/min. The auto sampler was set for desired sample frequency, usually 30 minute intervals. The well on the Gamma Cell was closed and lowered into the radiation field. Simultaneously, the auto sampler is activated to synchronize analyses of the gas chromatograph with the initiation of sample irradiation.
- (10) The system was normally run for 24 hours.

EXPERIMENTAL RESULTS

Eight different solids (See Table 1) were tested for performance as catalysts in individual experiments. All experiments were performed with 100 cc H_2O and .75 grams of the catalyst with the exception of run #119 which .25 grams of MgO was used. Most runs were for 24 hours with automatic sampling at 30 minute intervals. The results of these runs were graphed and are shown as Figures 7-17. The graphs show integrator count (C) versus time in the gamma radiation field for a corrected actual nitrogen transport flow rate of 46.3cc/min. (50cc/min flow rate indicated on the flow meter is actually 46.3cc/min. See calibration of flow meter.) Figures 18-20 represent runs with 100cc H_2O in the absence of solids. The latter were used for baseline data, as they indicate quantities of H_2 generated from the interaction of only radiation with water.

ANALYSIS OF DATA

A 300 minute interval was selected from each run. This selection was based on maximum average hydrogen detection. The intervals selected are indicated by arrows on the Figs. 7-20 in the previous section. The integrator counts were averaged for each run in the 300 minute interval (See Table 2). Average values ($\bar{C}_A$) for different runs but using the same catalyst were also averaged and the results are shown on Table 3. The uncertainties ΔC_A in the integrator count were obtained from the calibrations of the gas chromatograph and integrator, except for the baseline data, where the standard deviation was used for the uncertainty. A plot of hydrogen yield (ppm), versus band gap is shown in Figure 21.

Table 1 - Radiation Catalysis Tests

<u>Run Number</u>	<u>Catalyst</u>	<u>Grams</u>	<u>(cc) H₂O</u>	<u>Number of Points</u>	<u>C_A* Average Counts</u>
118	---	---	100	10	4908.30
132	---	---	100	10	4706.71
139	---	---	100	10	5008.00
121	MoO ₃	.75	100	10	4589.40
127	MoO ₃	.75	100	10	4623.80
134	In ₂ O ₃	.75	100	10	4742.80
120	TiO ₂	.75	100	14	5091.71
138	TiO ₂	.75	100	10	5072.50
128	V ₂ O ₅	.75	100	10	5335.60
119	MgO	.75	100	10	5578.30
137	MgO	.25	100	10	5824.20
136	Sb ₂ O ₃	.75	100	10	5850.70
131	HfO ₂	.75	100	10	6221.90
130	SnO ₂	.75	100	10	6643.60

*C_A = average counts for 300 minutes

The integrator counts can be converted to parts per million (ppm) of Hydrogen (Table 3).

where $\text{ppm} = \bar{C}_A / K$ $K = 19.3 \pm 0.6$ (See Appendix II Calibration of G. C. and Integrater) and $\Delta \text{ppm} = \sqrt{\left(\frac{\Delta C_A}{K}\right)^2 + \left(\frac{C_A}{K^2}\right)^2 (\Delta K)^2}$

$G_{(H_2)}$ value can also be obtained. ($G_{(H_2)}$ is the amount of H_2 molecules formed per 100 ev. deposited in the water.)²¹

$$G_{H_2} = 100 \frac{n_H F_{RA}}{D}$$

and $\Delta G_{H_2} = 100 \sqrt{\left(\frac{F_{RA}}{D}\right)^2 (\Delta n_H)^2 + \left(\frac{n_H}{D}\right)^2 (\Delta F_{RA})^2 + \left(\frac{n_H F_{RA}}{D^2}\right)^2 (\Delta D)^2}$

where n_H = number of H_2 molecules/cc

F_{RA} = actual flow rate = 46.3 ± 0.9 cc/min

D = dose rate = 3.12×10^5 rads/hr $\approx 3.25 \times 10^{19} \pm 0.03 \times 10^{19} \frac{\text{ev}}{\text{gm}}$ for H_2O .

These values are shown in Table 3.

Table 2. Average Counts for a 300 Minute Period

<u>Run #</u>	<u>Catalyst</u>	<u># of points</u>	<u>Average Count</u>
118	--	10	4908.30
132	--	10	4706.71
139	--	10	5008.00
121	MoO ₃	10	4589.40
127	MoO ₃	10	4623.80
134	In ₂ O ₃	10	4742.80
120	TiO ₂	14	5091.71
138	TiO ₂	10	5072.50
128	V ₂ O ₅	10	5335.60
119	MgO	10	5578.30
137	MgO	10	5824.20
136	Sb ₂ O ₃	10	5850.70
131	HfO ₂	10	6221.90
130	SnO ₂	10	6643.60

Table 3. Values for n_H , ppm, G_{H_2} , for the Catalysts

Catalyst	Count $\bar{C}_A$	ΔC_A	n_H ($\times 10^{15}$)	Δn_H ($\times 10^{15}$)	ppm $\bar{C}_{A/K}$	Δppm	$G_{(H_2)}$	ΔG_{H_2}	Band Gap* ev
Baseline	4874.3	153.5	2.4	0.1	252.6	11.2	0.35	0.02	---
MoO ₃	4606.6	129.3	2.3	0.1	238.7	10.0	0.29	0.02	2.8
In ₂ O ₃	4742.8	129.3	2.4	0.0	245.7	10.2	0.34	0.02	2.619
TiO ₂	5082.1	129.3	2.5	0.1	263.3	10.6	0.36	0.02	3.0
V ₂ O ₅	5335.6	129.3	2.7	0.1	276.5	10.9	0.38	0.02	2.34
MgO	5701.3	129.3	2.8	0.1	295.4	11.4	0.40	0.02	7.77
Sb ₂ O ₃	5850.7	129.3	2.9	0.1	303.2	11.6	0.42	0.02	3.31
HfO ₂	6221.9	129.3	3.1	0.1	322.4	12.1	0.44	0.02	5.55
SnO ₂	6643.6	129.3	3.3	0.2	344.2	12.6	0.47	0.02	4.3

*"Compilation of Energy Band Gaps in Elemental and Binary Compound Semiconductors and Insulators", 1973 00. 163-199. 22

Figure 7 — $\text{H}_2\text{O} + \text{M}_0\text{O}_2$ (run #127)

Figure 8 — $\text{H}_2\text{O} + \text{M}_0\text{O}_2$ (run #121)

Figure 9 — $\text{H}_2\text{O} + \text{In}_2\text{O}_3$ (run #134)

Figure 10 — H₂O + TiO₂ (run #138)

Figure 11 — H₂O + TiO₂ (run #120)

Figure 12 — H₂O + V₂O₅ (run #128)

Figure 13 — H₂O + MgO (run #137)

Figure 14 — H₂O + MgO (run #119)

Figure 15 — $\text{H}_2\text{O} + \text{Sb}_2\text{O}_3$ (run #136)

Figure 16 — $\text{H}_2\text{O} + \text{HfO}_2$ (run #131)

Figure 17 — H₂O + SnO₂ (run # 130)

Figure 18 — H₂O (run #139)

Figure 19 — H₂O (run #132)

Figure 20 — H₂O (run #118)

CONCLUSIONS

Calculation of O-H bond energy

Heat of formation of $\text{H}_2\text{O}(\text{g})$ from elements = 57.82 Kcal/mole
 Heat dissociation of H_2O (103.4 Kcal/mole) and O_2 (118.2 Kcal/mole)

Heat of reaction: $2\text{H} + \text{O} \rightarrow \text{H}_2\text{O} = 220.3 \text{ Kcal/mole}$

Removal of the first H atom for H_2O probably requires more energy than removal of second. Assume equality as first approximation, therefore bond energy of O-H = 110.2 Kcal/mole. (Pauling, 1945, pp 52-53)²³

$110.2 \text{ Kcal/mole} (1/6.02 \times 10^{23} \text{ molec./mole}) = 1.83 \times 10^{-22} \text{ Kcal/molec.}$

$(1.83 \times 10^{-22} \text{ Kcal/molec}) (4.186 \times 10^{10} \text{ erg/Kcal}) (6.242 \times 10^{11} \text{ eV/erg}) = 4.78 \text{ eV/molec.}$ (where molec refers to the OH bond)

A change in hydrogen yield (from radiation - induced water decomposition) was observed to relate to the forbidden band gap (E_g) of the solid used as a catalyst. Fig. 21 plots average measured hydrogen values as function of E_g for the materials tested. Baseline data, or that measured with water alone is in general agreement with those reported by numerous workers (Draganic and Draganic 1971)²⁴. The accepted G value for hydrogen for gamma-irradiated water is 0.45 molecules per 100 eV. The thrust of this study was to examine possibilities of increasing hydrogen yields over baseline.

Our experiments indicate that a maximum yield of the amount of hydrogen produced appears to occur when the band gap of the catalyst is greater than 3.31 electron volts and less than 5.55 electron volts. Water decomposition decreases and may approach baseline values when the band gap is equal to or greater than 5.55 electron volts. Solids with band gaps less than 3.0 electron volts appear to have no effect on water decomposition.

Figure 21 — Band gap versus H₂ yield (ppm)

The amount of hydrogen measured for these are within experimental error of baseline data.

Hydrogen yield using SnO_2 (band gap 4.3 eV) was 344.2 ppm compared, with baseline values of 252.6 ppm. This oxide produced the greatest yield of hydrogen in these experiments, suggesting that the maximum hydrogen yield may occur with a solid whose band gap energy lies between 3.31 and 5.55 electron volts. This is roughly equivalent to the O-H bond energy of 4.78 eV.

FUTURE WORK

Prior to exploring the significance of these finds, additional runs will be made with fresh batches of solid materials. Following this, new binary solids whose E_g 's are in the range of 4-6eV will also be tested to determine if the band gap is basic to the process.

Most importantly, thin films both undoped and doped will be tested for their performance in terms of enhanced hydrogen yields. Doped solids will also be tested.

The Principal Investigator devoted approximately 25% time to this project.

APPENDIX I

Tabulation of Experimental Data

The following tables list the data obtained. The values are for transport gas (N_2) flow rate of 46.3 ± 0.9 cc/min. and a gamma radiation dose rate of $3.12 \pm 0.03 \times 10^5$ rads/hr.

12

<u>Run Number</u>	<u>118</u>	<u>121</u>	<u>127</u>
<u>Catalyst</u>	<u>NONE</u>	<u>MoO₃ (0.75g)</u>	<u>MoO₃ (0.75g)</u>
<u>Elapsed time between measurements</u>	<u>Integrator Count (C)</u>	<u>Integrator Count (C)</u>	<u>Integrator Count (C)</u>
30	5451	4461	4343
30	4855	4430	5018
30	4942	4785	4946
30	4529	4412	4834
30	4998	4556	4543
30	4745	4370	4659
30	4582	5487	4480
30	4744	4485	4423
30	4451	4435	4306
30	4570	4428	4421
30	4811	4436	4608
30	4770	4500	4505
30	4667	4638	4511
30	4546	5197	4477
30	4594	4405	4559
30	4864	4322	4447
30	4690	4296	4478
30	4876	4372	4284
30	4820	4387	4458
30	5118	4301	4284
30	5231	4528	4316
30	5060	4235	4218
30	4912	4420	4113
30	4803	4380	4092
30	4725	4366	4239
30	4948	4299	4062
30	4649	4336	4049
30	4715	4620	4125
30	4922	4452	4154
30	4840	4598	4055
30	4822	4448	4183
30	5129	4212	4025
30	4813	4293	4183
30	4900	4221	4148
30	4908	4609	4192
30	5087	4686	4227
30	4804	4575	4349
30	4814	4606	4228
30	5054	4395	4382
30	4698	4529	4199
30	4710	4335	4413
30	4980	4434	4367
30		4236	4375
30		4559	4173
30		4449	4210
30			4283
30			4252
30			4275
30			4050
30			4181

<u>Run Number</u>	<u>128</u>	<u>130</u>	<u>131</u>
<u>Catalyst</u>	<u>V₂O₅ (0.75g)</u>	<u>SnO₂ (0.75g)</u>	<u>HfO₂ (0.75g)</u>
<u>Elapsed time between measurements</u>	<u>Integrator Count (C)</u>	<u>Integrator Count (C)</u>	<u>Integrator Count (C)</u>
30	7447	9473	1175
30	6177	9993	3435
30	5589	10375	3331
30	5256	9524	4064
30	5064	4223	4131
30	5023	6365	4395
30	4730	4324	4526
30	4697	5667	4898
30	4638	4258	5072
30	4734	4430	5474
30	4515	4678	5406
30	4767	4417	5692
30	4400	4457	5580
30	4775	4469	6039
30	4290	4573	5884
30	4244	4674	5931
30	4425	4509	6070
30	5163	4479	6002
30	4109	4469	6078
30	4188	4433	5836
30	4264	4421	5867
30	4227	4375	6015
30	4476	4399	6250
30	4420	4777	6250
30	4157	4610	6086
30	4017	4745	6371
30	4145	4606	6294
30	4109	4826	6337
30	4006	4495	6110
30	4050	4734	6104
30	4186	4417	6185
30	4083	4661	6192
30	4259	4365	5827
30	4042	4587	6176
30	4065	4434	6288
30	4206	4595	6011
30	4040	4766	5957
30	4124	4259	5838
30	3958	4298	5792
30	4165	4494	6043
30	4234	4446	5862
30	4180	4487	6167
30	4321	4442	5697
30	4024	4821	5601
30	3978	4417	5584
30		4495	5531
30		4289	
30		4218	
30		4352	
30		4625	
30		4094	

<u>Run Number</u>	<u>132</u>	<u>134</u>	<u>136</u>
<u>Catalyst</u>	<u>NONE</u>	<u>In₂O₃ (0.75g)</u>	<u>Sb₂O₃ (0.75g)</u>
<u>Elapsed time between measurements</u>	<u>Integrator Count (C)</u>	<u>Integrator Count (C)</u>	<u>Integrator Count (C)</u>
30	3241	4515	1940
30	3722	4817	6222
30	4048	4923	6674
30	4019	5022	7001
30	4161	4877	6226
30	4306	4948	5897
30	4452	4687	5728
30	4476	4783	5383
30	4606	4449	5222
30	4604	4407	5052
30	4568	4077	5102
30	4713	3980	5093
30	4753	3906	4869
30	4739	3922	4800
30	4775	3760	4440
30	4638	3462	4603
30	4767	3369	4618
30	4828	3233	4647
30	4682	3347	4543
30	4729	3643	4550
30	4502	3676	4471
30	4612	3501	4582
30	4428	3722	4477
30	4649	3838	4612
30	4506	3866	4464
30	4631	4017	4585
30	4587	4160	4461
30	4690	3884	4464
30	4608	4048	4585
30	4489	3902	4461
30	4579	3984	4530
30	4614	4107	4425
30	4435	3996	4492
30	4177	3906	4383
30	4263	3962	4378
30	4477	4132	4393
30	4282	3977	4272
30	4244	4131	4264
30	4487	4939	4207
30		4186	4215
30		4055	4147
30		4072	4113
30		4139	4307
30		4061	4293
30		4144	4436
30		4228	4277
30		4983	4330
30			4274
30			4299

↓
4410
4350
4269
4372
4258

↗

<u>Run Number</u>	<u>137</u>		<u>138</u>
<u>Catalyst</u>	<u>MgO (0.25g)</u>		<u>T₁O₂ (0.75g)</u>
<u>Elapsed time between measurements</u>	<u>Integrator Count (C)</u>	<u>Elapsed time between measurements</u>	<u>Integrator Count (C)</u>
5	474	7	1386
6	4604	7	6076
7	5485	30	4523
30	5478	30	4539
30	5627	30	4823
30	5606	30	4828
30	6182	30	4829
30	5681	30	4864
30	5648	30	4898
30	5687	30	5027
30	5712	30	5470
30	5796	30	5063
30	5807	30	5022
30	5978	30	5051
30	5981	30	5018
30	5965	30	5150
30	5818	30	5046
30	5748	30	4980
30	5715	30	4849
30	5785	30	4759
30	5595	30	4600
30	5581	30	4564
30	5500	30	4393
30	5406	30	4284
30	5399	30	4184
30	4385	30	4075
30	5336	30	4048
30	5253	30	4012
30	5304	30	4165
30	5234	30	4052
30	5194	30	4100
30	5250	30	3995
30	5306	30	3939
30	5317	30	4030
30	5186	30	4082
30	5182	30	4005
30	5237	30	3901
30	5350	30	4048
30	5357	30	4068
30	5261	30	3933
30	5216	30	4075
30	5216	30	3509
30	4945	30	3903
30	4949	30	3936
30	4908	30	4015
		30	3903

Run Number139CatalystNONEElapsed time
between
measurmentsIntegrator
Count (C)

30	3414
30	3539
30	3726
30	4116
30	4230
30	4395
30	4413
30	4484
30	4685
30	4813
30	4943
30	4788
30	4947
30	5061
30	1800
30	5047
30	5052
30	4934
30	4971
30	4926
30	4894
30	4882
30	4936
30	4978
30	4776
30	4840
30	5576
30	4836
30	5434
30	4721
30	4685
30	4765
30	4765
30	4825
30	4672
30	2794
30	4604
30	3821
30	4840
30	4544
30	4533
30	4638
30	4497
30	4489
30	4521
30	4497
30	4814
30	4634
30	4695
30	4719

1. The Gamma Cell

The standard Fricke dosimetry method was used to determine the ^{60}Co radiation flux and thus calibrate the gamma cell. The unit used was kindly made available to this project by the Denver V.A. Hospital. This method is based on the radiation induced oxidation of ferrous to ferric ion, and the extent of oxidation is related quantitatively to the gamma energy deposited in the water solution.

The preparation of the chemical solution was as follows:

- 1) A 250 ml solution of 0.4 M H_2SO_4 was prepared.
- 2) Added to this solution was a few cc of 0.001 m NaCl .
- 3) Oxygen was then bubbled through the solution for ten minutes.
- 4) Five grams of $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (ferrous ammonium sulfate) were then dissolved in the solution.

Eight labeled sealed glass vials were then filled with 15 ml each of the above ferrous solution. Two of the vials were placed in the gamma cell for a radiation exposure of precisely two minutes. The vials then replaced with two fresh vials, exposed for four minutes. The above procedure was then repeated with fresh vials for six and eight minutes.

All eight vials were then analyzed to determine the absorbance values of ferric ions relative to an unirradiated sample of the solution. The absorbance was measured with a Beckman DU II spectrophotometer using standard 1 cm silica cells at 304 m μ . At this wavelength the ferrous ions have negligible absorbance. The absorbance values for the samples are listed in Table 1.

The absorbed dose $D(\text{rads})$ is calculated from the following formula

for a 0.4 M H_2SO_4 , 1 cm absorption cells and $G(\text{Fe}^{3*}) = 15.6$. (The Radiation Chemistry of Water, Draganic and Draganic).

$$D = 2.75 \times 10^4 \times \Delta A \quad (1)$$

where ΔA is the relative absorbance. The optical density measurements are performed at 25°C, however, temperature correction factor of 0.69% per degree is required. Then:

$$D(\text{rads}) = (2.75 \times 10^4) (\Delta A) (1 + 0.0069(T-25)) \quad (2)$$

Table 2 lists the results obtained using equation 2.

Attenuation caused by the glass vial was also considered.

$$I = I_0 e^{-ux} \quad (3)$$

I_0 = unattenuated dose rate

I = attenuated dose rate = 3.4×10^5 rads/hr.

u = glass linear absorption coefficient for gamma rays of 1.5

MeV = 0.14 cm^{-1} .

x = thickness of attenuator = 0.15 cm.

The unattenuated dose rate $I_0 = 3.5 \times 10^5$ rads/hr.

The attenuation due to the glass vessels used in the experiments was also taken into consideration. Using equation (3) with $x = 0.23$ cm, the dose rate in the radiation vessel was found to be 3.4×10^5 rads/hr.

The result was compared to the flux measurement of the gamma cell made on November 4, 1976. The unattenuated average dose rate was found at that time to have a value of 4.0×10^5 rads/hr.

$$I = I_0 e^{-\lambda t} \quad (4)$$

The decay constant λ , for CO^{60} with a half life of 5.3 years is

equal to 0.13 yr^{-1} . The time elapsed T , since I_0 was measured, was taken to be 11/12 year, yielding a value of $I = 3.5 \times 10^5$ rads/hr,

*G value is a term measuring the efficiency of a radiation-induced reaction. It is the number of molecules formed or destroyed per 100eV of energy absorbed.

in agreement with the present unattenuated measurement.

Table 1 Absorbance Values

<u>Sample</u>	<u>Exposure Time (sec.)</u>	<u>Absorbance (ΔA)</u>	<u>Temperature = 26°C</u>
*1	120	0.082	
*2	120	0.175	
3	240	0.808	
4	240	0.820	
5	360	1.230	
6	360	1.230	
7	480	1.650	
8	480	1.650	
*1	120	0.100	
*2	120	0.186	

*Samples #1 and #2 were reanalyzed but were not used in the calculation of the dose rate because of their inconsistency in absorbance values.

Table 2 Dose Rate Values

<u>Sample</u>	<u>Exposure time (min.)</u>	<u>D(rads)</u>	<u>D(rads/hr.)</u>
3	4	2.2×10^4	3.4×10^5
4	4	2.3×10^4	3.4×10^5
5	6	3.4×10^4	3.4×10^5
6	6	3.4×10^4	3.4×10^5
7	8	4.8×10^4	3.4×10^5
8	8	4.8×10^4	3.4×10^5

Since ^{60}Co has a half life of 5.3 years it will be necessary to correct the dose rate with time using equation (4). The results can be found in Table 3.

Table 3 Change in Radiation Dose with Time

<u>Time (months)</u>	<u>Radiation Dose (rads/hr)</u>	<u>Percent of Initial Dose Rate</u>
0	3.4×10^5	0
1	3.4×10^5	-
2	3.4×10^5	-
3	3.3×10^5	97
4	3.3×10^5	97
5	3.2×10^5	95
6	3.2×10^5	95
7	3.2×10^5	95
8	3.1×10^5	92
9	3.1×10^5	92
10	3.0×10^5	90
11	3.0×10^5	90
12	3.0×10^5	90

2. Gas Chromatograph and Integrator

Two calibration gases were obtained from Union Carbide, Los Angeles, California. Calibration gas #1 was a $45.7 \pm 3\%$ ppm mixture of hydrogen in nitrogen. Calibration gas #2 was a $481 \pm 3\%$ ppm mixture of hydrogen in nitrogen. (Certification of analyses was made by the vendor.) Several runs of these gases were made in order to calibrate the output of the gas chromatograph and integrator. The results of these runs are shown in Table 4.

Since the gas chromatograph measures actual number of molecules and not ppm directly, an error in the number of H_2 molecules per unit volume is introduced due to variations in temperature and pressure. United States Weather Bureau statistics indicate that maximum and minimum pressure in the Denver area for the last year was 63.88 and 60.96 cm of Hg respectively. Using the pressure as $62.42 \text{ cm of Hg} \pm 1.46$ and the temperature as $40.0^\circ\text{C} \pm .001^\circ\text{C}$ and using the ideal gas law, the total number of molecules per cubic centimeter (n/v) is $1.92 \times 10^{19} \pm .05 \times 10^{19}$. To convert counts (C) from the integrator to actual number of hydrogen molecules per cubic centimeter (n_H), the following equation was used.

$$n_H + \left(\frac{n}{v}\right) \frac{C}{K106} \left(\frac{1}{2}\right) = 0.60 \times 10^{12} \left(\frac{C}{K}\right), \text{ where } K = C/\text{ppm}$$

The factor of $1/2$ is introduced because the gas chromatograph analyzes a 2 ml sample.

Table 4. Results of Calibration Gas Runs

Calibration Gas H ₂ in N ₂ (ppm)	Run #	# of Samples	$\bar{C}_c$ Mean Value of Counts	ΔC_c	K Counts/ppm K=C _c /ppm	ΔK^*
45.7 $\pm$ 3%	102	45	769.38	109.62	16.8	2.5
45.7 $\pm$ 3%	103	41	883.97	110.33	19.3	2.5
45.7 $\pm$ 3%	112	25	796.68	112.35	17.4	2.5
481 $\pm$ 3%	114	38	9277.84	129.29	19.3	0.6
481 $\pm$ 3%	116	15	8661.87	220.96	18.0	0.7

$$*\Delta K = \left[\left(\frac{\partial K}{\partial \bar{C}_c} \right)^2 (\Delta C_c)^2 + \left(\frac{\partial K}{\partial \text{ppm}} \right)^2 (\Delta \text{ppm})^2 \right]^{1/2}$$

3. Flow Meter

A soap bubble meter was used for calibration of the flow meter. The bubble meter was made from a 250 ml graduated burette with a rubber bulb on the bottom and a gas inlet fitting above the bulb on the side. The gas enters the bubble meter and when the bulb is squeezed a soap bubble is formed and travels up the tube at the gas flow rate. A stop watch was used to time the travel of the bubble. By knowing the time and the volume displaced during the bubble's travel, the flow rate can be calculated. (See Table 5.)

Table 5. Calibration of Flow Meter

n	$\bar{V}_D$	$\bar{T}$	ΔT	V_D	$\bar{F}_{RA}$	ΔF_{RA}	F_{RM}
5	50.0	35.2	0.2	0.5	85.2	.98	83
5	50.0	39.4	0.1	0.5	76.1	.79	75
5	40.0	40.8	0.1	0.5	58.8	.75	60
5	30.0	34.4	0.2	0.5	52.4	.92	55
5	30.9	38.9	0.3	0.5	46.3	.86	50
5	30.0	40.6	0.5	0.5	44.3	.92	48
5	30.0	43.4	0.2	0.5	41.5	.72	45
5	30.0	49.4	0.4	0.5	36.4	.70	40
5	30.0	84.0	0.2	9.5	21.2	.36	25
5	30.0	90.8	0.3	0.5	19.8	.34	23
5	20.0	73.4	1.4	0.5	16.4	.51	20

V_D = Volume displaced by soap bubble measured in cc.

T = Time for bubble to displace volume V in seconds

F_{RA} = Actual flow rate of gas measured in cc/min.

F_{RM} = Reading of flow meter in cc/min.

n = number of measurements

NOW $\bar{F}_{RA} = 60 \bar{V}_O / \bar{T}$ (cc/min)

$$\Delta T = \left[(T_c - \bar{T})^2 / (n-1) \right]^{1/2}$$

$$\Delta F_{RA} = \left[\left(\frac{\partial F_{RA}}{\partial V} \right)^2 (\Delta V)^2 + \left(\frac{\partial F_{RA}}{\partial T} \right)^2 (\Delta T)^2 \right]^{1/2}$$

BIBLIOGRAPHY

1. N.B. Hannay, Editor, Treatise on Solid State Chemistry, Vol. 5B, Surfaces II, Plenum Press, New York, 1976 pp. 59-73.
2. L.S. Polak and S.Y. Pshezhetsky, "Heterogeneous Processes in Radiation Catalysis", Pure and Appl. Chem. 10, No.4, p. 441 (1965).
3. R. Coekelbergs, A. Cruz and A. Frennet, "Advances in Catalysis", Vol. 13, p. 55, Academic Press, New York, 1962.
4. O.V. Krylov, "Special Features of Catalysis of Magnesium Oxide etc.", Problemy Kineticki i Katalize. XV, Mekhanism i Kineticka Geterogennykh Reaktsiy, Izd. vo Nauka, Moscow, 1973, pp. 85-94, (in English: AD/A-000 186, Foreign Technology Div., W-P Air Force Base, Ohio, 4 October 1974).
5. D.G. Klissurski, "On the Approximate Correlation Between the Bonding Energy of Oxygen in Metal Oxides and the Width of their Forbidden Zones", Solid State Comm., vol.15, pp. 1789-1792 (1974).
6. O.B. Krylov, "Catalysis by Nonmetals", Chapter 1, pp. 6-24, Academic Press, New York, 1970.
7. D. Frankel, "Surface Space Charge Layers in Solids", in "Solid State Surface Science", Vol. 3, Marcel Dekker, N.Y., 1973.
8. A. Many, Y. Goldstein and W. Grover, Semiconductor Surfaces, North Holland Publishing Co., 1965.
9. P. Mark, et al., "The Role of Surface States in Metal Semiconductor Barrier Formation", Applied Phys. Lett., Sept. 1975.
10. J. Phillips and J. Andrews, "Chemical Bonds and Heats of Formation at Metal-Semiconductor Barriers", Phys. Rev. Lett., July 1975.
11. H. Matare, Defect Electronics of Semiconductors, Wiley Interscience, N.Y. 1971.
12. H. Webb, R. McIntyre and J. Conrade, "Properties of Avalanche Photodiodes", RCA Review, Vol. 35, 1974.
13. M. Green and M. Lee, "Simple Complexes on Semiconductor Surfaces", in "Solid State Surface Science", Vol. 1, Marcel Dekker, N.Y. 1969.
14. J. Riviere, "Work Functions; Measurements and Results", Ibid, p. 179.

15. J. Horiuty and Tomigyko Toya, "Chemsorbed Hydrogen", Ibid. p. 2.
16. P. Gill and P. Chen, "Physics of Xerographic Photoreceptors", "Applied Solid State Sciences", Vol. 6, January 1976.
17. T. Rokoske and P. Budenstein, TSC Analysis of DC Conduction Mechanisms in Thin Films of S_1 , MgF_2 and Teflon, in Electrets, M. Pearlman, Ed., The Electrochemical Society, 1973.
18. F. Aris, D. Huges and T. Lewis, Trap Limited Currents, Charge Storage and Trap Energies in Anodic Tantalum Oxide Film, Ibid. p. 331.
19. J.B. DuBow, D.E. Berk, J.R. Sites, "Solar Cells of Indium Tin Oxide on Silicon", Presented at IEEE International Electron Device Conf., Washington, DC, Dec. 1975.
20. Jarzebski, "Oxide Semiconductors", Pergamon Press, 1973.
21. V.D. Maiboroda, "Equilibrium concentrations of molecular products on steady-state water radiolysis", Akad. Navuk B. SSR, Ser. Fiz - Energ. Navuk 1974 (4) 34-7, Chem. Abst. 82, 162925a (1975). (See also: A.O. Allen, Radiation Chemistry of Water and Aqueous Solutions. D. Van Nostrand & Co., Princeton, 1961.)
22. J. Phys. Chem. Ref. Data, Vol. 2, No 1, pp. 163-199, 1973.
23. L. Pauling, The Nature of the Chemical Bond. Cornell University Press, Ithaca. 1945.
24. Z.O. Draganic and I.G. Draganic. Radiation Chemistry of Water. Academic Press, N.Y. 1971

ACKNOWLEDGEMENTS

Most of the experimental work on this project was performed by George R. Goebel, graduate student in the Physics Department, Colorado School of Mines. The research done under this grant was in partial fulfillment of his Master's Degree requirements at CSM. Appreciation is expressed to Professors Don Williamson and William Law, Physics Department faculty, and Dr. Agnes Wang, Research Associate, CSM.

Special appreciation is given to the Veterans Administration Hospital, Denver, for making their Gamma Cell available to this project, and particularly to Richard Troll, Radiation Safety Officer at the VA for his support.

The principal investigator also wishes to thank Pam Davis and Barbara LaSasso, Colorado Energy Research Institute, for typing this manuscript.

Finally, appreciation is expressed to the Colorado Energy Research Institute and the Colorado School of Mines for their support of this program.

J. G. Morse
Associate Professor (Adj)
Physics Department, CSM
Principal Investigator

APPENDIX A

INTRODUCTION

This report outlines the progress made during the past year under the program "Hydrogen and Methane Synthesis using Radiation Catalysis." Efforts have been made to fulfill contractual obligations in five areas under the above program. One was to supply appropriate catalyst materials to Colorado School of Mines for studying the reactions proposed. Another was to characterize the electrical properties of these catalysts. A third was to study the effects of gamma irradiation on the candidate catalyst materials. A fourth was to interpret the reaction rate data from a solid-state device and solid-state materials viewpoint. The fifth was to compare and contrast the hydrogen synthesis results obtained from optical excitation with that obtained using gamma ray excitation. The research team that has been utilized on this project is particularly well suited to this task and has contributed to the high rate of understanding that has been attained during the past year. This group consists of a physical chemist, Dr. Krishnan Rajeshwar; a physicist, Paramjit Singh; a research technician, Bob Rosenvold; and a solid-state device physicist, Dr. Joel DuBow. Also contributing to the project is an expert in semiconductor-insulator interfaces, Dr. Samares Kar from IIT in India. The availability of these personnel has been a result of the solar energy and oil shale research also going on at CSU. However their presence has been instrumental in helping both projects.

During the early part of the program efforts were made to understand the mechanisms of catalytic hydrogen formation at semiconductor electrodes. As was discussed in the proposal, it is important to differentiate between

electron transfer by tunneling through the interfacial layer and between transfer caused by electron removal from the solid directly. In the former case the energy band gap would be a critical parameter, and in the latter case the electron affinity would be critical. A result of the studies at CSU show that, indeed, both parameters are important. It soon became clear that a heterostructure device model was appropriate for describing the behavior of these systems. Therefore, catalyst candidates needed to be selected with energy gap larger than the redox potential of the water dissociation (1.23 eV) and that the energy gap not be so large such that the electron affinity be too small so that charge transfer in the bulk semiconductor would be hindered by very low mobility and that band bending at the surface of the semiconductor still be appreciable. A set of oxide powders was selected with appropriate electron affinity and band gap considerations in mind.

The electrical properties of these catalysts were obtained prior to irradiation. In this regard, an apparatus needed to be constructed to obtain the electrical properties of these oxides and their frequency dispersion. Since electrical data on powders is not readily available for many materials, and is a strong function of packing fraction, care had to be taken in the construction of sample cells to eliminate fringing effect and to obtain accurate packing fraction data so as to compare the data obtained on powders with available data on bulk material. Data were obtained on the dielectric constant and electrical conductivity as a function of frequency for the catalyst powders. Because of conflicting constraints between the dielectric measurements, which work best with larger samples, and the catalysis experiments which seem to work best with smaller samples, data on irradiated samples lagged behind that of the unirradiated

samples.

For the latter parts of this research, thin film catalyst materials were required. These films would be easier to characterize and provide more meaningful data on transport properties, band gaps, and surface areas. To produce these films, which would consist of a combination of insulating, semiconducting, and conducting materials, an ion beam deposition system was obtained and set up. This system can sputter a wide range of materials and material compositions from pressed powder substrates. Preliminary films using this system have been obtained. In the next contract period other films will be obtained and their electrical properties characterized. The substrates to be used include glass and alumina. The use of thin films will also assist in better coordinating sample sizes with the catalyst experiments. One of the key achievements of the first contract period under this contract was obtaining an understanding of the mechanism of hydrogen evolution and electricity generation in optically illuminated electrolyte-semiconductor systems. Since most systems studied concern photochemical hydrogen and photochemical electricity generation, a comprehensive study was made of these systems. In principal, the gamma ray system should be identical to the photochemical system except that the input radiation is higher in energy and the resulting free carriers generated in the bulk of the sample have much higher energy than corresponding carriers generated with visible radiation. The added dimension of higher energy free carriers in the bulk and surface could give rise to an improved performance in gamma irradiated systems. Moreover the gamma sources do not suffer from periodic daily variations, insolation variations, and intensity limitations that conventional sunlight provides. The results of this study are contained in two articles. One article is a survey of

photo-electrochemical cells that have been studied to date. A review of existing analytical models and experimental results was assembled and will be published in the journal *Electrochimica Acta* this fall. The second article, which has been submitted to the *Journal of Applied Physics*, summarizes our insights obtained in preparing the first article by proposing a new theory for the operation of photo-electrochemical (PEC) solar cells. Although many previous workers have studied the semiconductor-electrolyte interface as well as the electrolyte-metal interface and the electrolyte double layer, none of these studies have considered the PEC solar system as a device, which in fact it is. A detailed consideration of the entire system, which requires closing the loop thermodynamically as well as physically modeling charge transfer from semiconductor through the double layer to the electrolyte and through the metal electrode through connecting wires via a battery to the semiconductor again indicates that the device may be modeled as a semiconductor-insulator-metal (MIS) system. The insulator system is the electrolyte with charge transport presumably by tunneling through its double layer. If the electrolyte is pure enough, then corrosion currents and dark currents are small and a stable cell with open circuit voltages approaching band gap voltages may be obtained. Preliminary experiments indicate that these open-circuit voltages are indeed obtained. The generation of high energy carriers using gamma irradiation will allow wider flexibility in choice of catalysts for hydrogen generation in a gamma electrochemical cell. In this regard the band gap may be chosen to minimize dark corrosion currents as well as with dissociation energy considerations in mind. In principal the gamma-ray electrochemical cell should function in a manner almost identical to the photo-electrochemical cell with gamma irradiation replacing optical

irradiation and higher energy carriers available in the semiconductor. This result is a recent one, and it would be interesting to try some of the catalysts selected using the recently gained understanding in a gamma cell configuration. It would also be worthwhile to investigate the effects of radiation upon the oxide semiconductor catalysts and in fabricating catalyst materials from multi-component oxides such as quaternary oxides which should be able to match band gaps to dissociation energies and electron affinity to redox potentials in the electrolyte. The future goals rest upon building upon the facilities and understanding obtained during the initial contract period and to obtaining a number of interesting results in the upcoming contract period.

Chapter 1 outlines the literature background and the planned correlation techniques to study the role of electronic structure of the catalyst in the decomposition of water. Chapter 2 describes the dielectric analysis technique that was specifically developed in this laboratory to study the dielectric properties of catalyst materials. Chapter 3 summarizes the application of this technique to catalyst powders. Chapter 4 describes the neutralized ion-beam deposition system that has been put together in this laboratory for the fabrication of thin-film catalyst materials.

The review article on the existing results on photo-electrochemical systems and the article on the theoretical modeling of semiconductor-electrolyte interfaces are found as Appendices A and B respectively.

CHAPTER 1
THE ROLE OF ELECTRONIC STRUCTURE OF THE CATALYST
IN THE DECOMPOSITION OF WATER

I. Introduction

Heterogeneous catalysis comprises the phenomenon of the enhancement of the rates of chemical conversions in fluids by the presence of solid surfaces, which are called catalysts. The categories of elementary processes customarily used to analyze heterogeneous catalysis can be listed as follows:

- 1) Diffusion of reactants to the surface.
- 2) Chemisorption of at least one of the reactants on the surface.
- 3) Surface diffusion of chemisorbed reactants and subsequent surface reaction.
- 4) Desorption of products from the surface.
- 5) Diffusion of products from the surface.

The key step for many catalytic processes is Step 3, which is generally believed to involve the formation of surface intermediaries which decompose to yield the desired product(s).

The electronic approach to the understanding of catalysis in solids seeks a relationship between its catalytic activity and the bulk electronic properties of a solid, namely permeability, dielectric constant, conductivity, electron affinity, fermi energy, and the band gap. Wolkenstein (1,2) Weisz (3), Krylov (4) and others have developed electronic theories of catalysis on semiconductors.

Measurements of electrical conductivity have established that the chemisorption of gases and vapors on semiconductors is accompanied by electron transfer from the semiconductor to the chemisorbed gas or vice versa, or by localization of the charge carriers of the semiconductor between the gas and the semiconductor surface. The direction of this change is a clear

indication of the direction of electron transfer. Thus, the decrease in the conductivity of an n-type semiconductor as a result of chemisorption implies that the electrons have been transferred from the conduction band of the semiconductor to the chemisorbed gas or trapped in the chemisorbed atom. A decrease in the conductivity of a p-type semiconductor indicates an electron transfer from the chemisorbed gas to semiconductor. Although the electron transfer is in opposite directions in these two processes, both are accompanied by a depletion of carriers in the semiconductor and may be classified together as examples of depletive chemisorption. The converse situation of an increase in conductivity upon chemisorption implies that carriers have accumulated on the semiconductor surface. This type of chemisorption is called cumulative chemisorption.

The new theories are based on the concept that if chemisorption changes the number of charge carriers in the semiconductor, then it should be possible to influence the rate of reaction by varying the concentration of charge carriers whenever the charge transfer enters into the rate determining step of the catalytic process.

This idea was reinforced by initially successful attempts by Stone (5) to correlate the activity of a series of oxides for the decomposition of N_2O with their electrical transport properties. It had been established that the rate determining step for this reaction involves the uptake of an electron by the lattice (6). However, discussions by Garrett (7) and Garcia-Moliner (8) have clearly shown the extreme simplifications involved in these electronic theories of catalysis on semiconductors. Among these were the complete neglect of extrinsic surface states, the frequent assumption of complete ionization of the surface states induced by adsorption and the assumption that these states are always to be found in the forbidden

gap between valence and conduction bands. As more of these simplifications are removed, more detailed knowledge of the semiconductor surface is necessary for a quantitative test of the theory. In the absence of such tests, only a qualitative confirmation of the relation between reaction rate and conductivity is possible. Chon and Prater (9) have related measurements of the rate of CO oxidation with measurements of the carrier concentration for ZnO. Quantitative confirmations may become possible with the use of single crystals for catalytic rate measurements, coupled with measurements of the electronic properties of the surface. The ambiguities introduced by the use of polycrystalline samples, such as surface segregation, spurious electric field, intergranular resistance, and shape effects, would then be removed.

II. Photoelectrolysis of Water Using Semiconductors

A. Literature Background

Sustained photoinduced conversion of H_2O to H_2 and O_2 using electrodes as photoassistance agents has been demonstrated by using TiO_2 (10) or sb-doped SnO_2 (11) or SrTiO_3 (12) as the photoelectrode. The photoassistance agent serves not only as a receptor for the incident light but also must channel the electronic excitation energy into pathways to achieve the desired chemical reactions. Some of the requirements which dictate the choice of the catalyst are:

- i) Semiconductive (n-type) and band gap ~ 3 eV or less (so that visible light can be used),
- ii) should not decompose (anodic dissolution) under illumination.

The efficiency of any electrode system used as a photoassistance agent in an optical to chemical energy conversion depends on the excitation wave-

length necessary to run the reaction and the energy required from an external power supply (other than the light). Band gap energy illumination produces electron hole pairs which participate in the electrochemical process. One of the advantages of the use of a semiconductor electrode in the study of the electrochemical reactions is the fact that the charge transfer process occurs via the energy bands. The optical absorption coefficient is also important for photoelectrolysis of water.

The n-type semiconductor electrodes of the rutile structure do not undergo decomposition upon irradiation when used as a photoelectrode in aqueous media. TiO_2 when reduced is an n-type semiconductor. SrTiO_3 has the simple cubic perovskite structure and when reduced is an n-type semiconductor.

Two types of photoelectrolysis cells have been used - heterogeneous cells consist of two different compartments connected by a KCl-agar salt bridge so that the electrodes could be immersed in different electrolytes; homogeneous cells - the TiO_2 (or SrTiO_3 , or Sb-doped SnO_2) and Pt electrodes are immersed in the same electrolyte. When the semiconducting electrode was illuminated, current flowed in the external circuit and O_2 and H_2 were liberated at the anode (semiconductor) and the cathode (generally platinum), provided that the photon energy exceeded 3.0 eV, the energy gap of TiO_2 . In Table 1.1, we briefly list some of the catalysts that have previously been used for the photoelectrolysis of water and the results obtained.

B. Energy Diagram of a Photoelectrolysis Cell

Figure 1.1 is a simplified energy diagram of a photoelectrolysis cell consisting of an n-type semiconducting anode, an acidic electrolyte and a metallic counter electrode. The two electrodes are connected through the external circuit, so that the Fermi level is the same for both.

TABLE 1.1

Catalyst Used and Its Band Gap	Reference	Comments
TiO ₂ 3 eV	10	Single crystal wafers were used, were reduced to increase the conductivity, quantum yield ~ 0.6 using a potential greater than 0.6 V with respect to standard colomel electrode (SCE)
TiO ₂ 3 eV	13	Doped TiO ₂ with tungsten. They were able to shift the onset of response by about 0.5 eV; unfortunately, the shift is towards the blue end of the optical spectrum.
SnO ₂ 3.5 eV	11	They used Sb-doped, n-type single crystals of SnO ₂ . SnO ₂ emerges as less efficient at room temperature because of higher band gap, but they were able to increase the low energy response of SnO ₂ by increasing the temperature although the effect was very small. External applied potential ~ 0.5 V with respect to SCE. They reported quantum efficiency ~ (0.27 ± .03).
SrTiO ₃ (3.2 - 3.4) eV	12	Used single crystals reduced at about 1100°C to make them semiconducting. They reported quantum efficiencies ~ 1 for photons of wavelength less than 3300 Å; when the applied voltage is ≥ 1.5 V. Longer wavelengths are not absorbed that efficiently. At lower applied voltages the quantum efficiency goes down.
TiO ₂ 3 eV	14	Single crystals and hot pressed disks were used. They reported quantum efficiency ~ 0.82 for single crystals and 0.6 for polycrystalline disks. They also used TiO ₂ films obtained by thermal oxidation of Ti foil. Thick films (greater than 7 μm) did better than thin films (less than 2 μm).

TABLE 1.1

(continued)

Catalyst Used and Its Band Gap	Reference	Comments
TiO ₂ 3 ev	15	Sensitization of TiO ₂ to visible light was accomplished by impurity doping. Using Cr doped anode, external bias ~ 0.6 V, they observed a quantum efficiency of 0.35 at 500 nm. A quantum efficiency of ~ 1 for Al doped TiO ₂ at 360 nm has been reported. They also tested TiO ₂ /CdS and TiO ₂ /CdSe anodes but these have the problem of photocorrosion. They also tried dye sensitization of TiO ₂ but the systems had the problem of instability.

Figure 1.1: Energy diagram of a photoelectrochemical cell

Because of the difference in work function between the semiconductor and the electrolyte, the energy bands of the semiconductor are bent at the surface so that the analog of a Schottky barrier exists at the semiconductor electrolyte interface. The semiconductor surface is irradiated by photons of energy at least equal to its energy gap.

The photon generated hole-electron pairs do not recombine but are separated by the electric field of the barrier, the electrons move away from the surface into the bulk of the semiconductor and then through the external circuit to the Pt cathode, where they discharge H_2 by the reaction:

While the holes remain at the surface of the semiconductor anode, where they can interact with the electrolyte to produce O_2 by the reaction:

Two conditions are necessary for efficient photoelectrolysis:

- 1) The energy bands at the semiconductor-electrolyte interface must be bent in order to separate the holes and electrons excited by the light.
- 2) The relevant electronic levels must line up; i.e., the hole states

of the anode with $\epsilon \geq \text{H}_2\text{O}/\text{O}_2$) and the fermi level ϵ_F with $\epsilon \geq (\text{H}^+/\text{H}_2)$ in order to permit transfer of holes at the anode and electrons at the cathode.

The amount of anode band bending, b_n , for a given fermi level, ϵ_F , is:

$$b_n = \epsilon_F - (\epsilon_F)_{fb}$$

$(\epsilon_F)_{fb}$, flat band potential, is the particular value of the fermi level for which the energy bands are not bent.

III. Effects of γ -Radiation on the Catalyst

On irradiation, additional imperfections will appear on the surface and these may be active in adsorption and catalytic processes. The changes induced in a solid by radiation may be classified by the nature of their relaxation.

- 1) Ionization and excitation of the crystal lattice, which do not last after irradiation has stopped.
- 2) Displacement of atoms. These effects persist long after irradiation has stopped, and yet disappear at a considerable rate when temperature is increased (annealing of defects).
- 3) Defects caused by chemical conversions induced by radiation in the solid such as decomposition of salts, reduction of oxidized forms, etc.

The crystal structure is affected when the radiation particle energies are close to the displacement threshold - atoms in their normal positions can be displaced into interstitial positions. Structure defects often arise when the energy of the radiation particles is not high enough to displace atoms by elastic collisions. In such a case the lattice destruction is due to ionization and excitation of electrons in the substance. Electron transi-

tions are known to occur in a solid irradiated by electrons or gamma rays. The electrons and holes in the conduction band may be trapped to form defects of some kind. Such defects at the surface of a solid may interact with the adsorbed molecules.

The appearance of radiation defects in crystals of semiconductors is accompanied by changes in the equilibrium concentration of charge carriers, due to the latter being trapped by defects, or to ionization. The likely mechanism by which the lattice defects come to the surface is one of diffusion of positive holes and translocation of electrons. A possible interaction between the adsorbed molecules and the non-equilibrium charge carriers trapped by surface centers is the recombination of holes and electrons in the vicinity of an adsorbed molecule, the energy evolved being thereby imparted to the molecule. The probability of this type of interaction is temperature dependent and goes down with temperature.

When γ rays of energy greater than 1 Kev are incident on the solid, the electrons carry away a large fraction ($\sim 99\%$) of the incident energy as kinetic energy. The energized particles are able to knock out atoms from their sites in the lattice, this remains a rather localized defect, since disrupted bonds are left behind by the free atom that has moved into an interstitial position (Frenkel defect) or to the crystal surface or an intercrystalline boundary (Schottky defect). The energy needed to break up lattice bonds is many times larger than that needed to displace atoms within the lattice after they are set free. Even though the energy needed for lattice disruption is of the order of a few eV, we need a very high energy electron to impart the required energy to the lattice because of the large difference in masses; e.g., for Ge the maximum energy transferred

to the lattice is 59 eV for a 1 MeV electron and the energy transferred seems to go down with the mass of the lattice.

It is very difficult to predict changes due to irradiation in semiconductors. The difficulty is caused by several unknowns:

- 1) There is no simple model for the energy levels of lattice defects.
- 2) The kind of interaction between defects and imperfections (impurity atoms and dislocations) already present before irradiation and the radiation induced defects. This may alter the energy level structure of the defects both during and after bombardment.
- 3) The relaxation of electronic effects (trapped minority carriers) after low temperature radiation that obscure relaxation processes involving defects.

Co γ rays have been known to produce defect levels in germanium, a donor level at 0.2 eV and an acceptor level at 1.26 eV.

The catalyst materials (polycrystalline and single crystals) we plan to use in the present investigation are selected on the basis of the criterion listed before i.e.:

- i) No anodic decomposition in aqueous solutions.
- ii) Semiconductors with band gaps $\sim 2 - 4$ eV (n-type).

We list the materials to be used and their energy band gaps and the corresponding wavelengths in Table 1.2.

Another reason for the selection of the above mentioned catalytic agents is the fact that their effectiveness has been demonstrated by previous investigations, and we would like to investigate as to what happens to their effectiveness in a radiation environment.

A reason for restricting the energy gap between 2 - 4 eV is that we want the catalysts to respond to the visible region of the electromagnetic

TABLE 1.2

<u>Catalyst</u>	<u>Band Gap</u>
Nb_2O_5	2.2 ev
TiO_2	3.0 ev
SrTiO_3	(3.2 - 3.4) ev
SnO_2	3.5 ev
ITO	3.65 ev

ITO is a mixture of SnO_2 and In_2O_3 . Although In_2O_3 is an insulator, if SnO_2 is added to it, the resulting polycrystalline material is found to be n-type semiconducting, and it responds to visible light. ITO is presently being used for fabrication of solar cells.

spectrum and since the dissociation of water theoretically needs only 1.23 eV, any energy in excess of this is a waste and goes into heating the system. Practically, it turns out that one needs some excess energy over the 1.23 eV to overcome some system impedances.

IV. Planned Correlation Techniques

- 1) An attempt will be made to correlate the catalytic activity with the electronic properties of the catalyst, so that we can look more closely at the electronic theory of catalysis on semiconductors as proposed by Krylov (4), Wolkenstein (2), and others. We plan to correlate the catalytic activity with the dielectric properties of the catalyst. The dielectric properties will be measured both before and after irradiation. They will be related to the hydrogen yield from the system.
- 2) X-ray diffraction studies will be made on the samples before and after irradiation to see if there has been any change in the particle size of the sample. We will look for any correlation between particle size and the catalytic activity.
- 3) For experiments using single crystals or thin films of the catalyst, Auger electron spectroscopy will be used to characterize the surface. We plan to use textured thin films (which have increased surface area due to texturing) of the catalyst and look for any effects that the surface area and surface structure has on the catalytic activity.

CHAPTER 2

DEVELOPMENT OF A NEW TECHNIQUE FOR DYNAMIC DIELECTRIC ANALYSIS

I. Introduction

Applications of dielectric analysis techniques in the thermophysical characterization of solids are well documented (16,17). Bridge methods (18) that are currently employed for dielectric measurements, are limited by the necessity of using different types of bridges for the various frequency ranges. Another disadvantage of these techniques is the inordinately long time required to make a set of measurements at different temperatures and frequencies. Therefore, a technique which would facilitate a rapid monitoring of the dielectric parameters of a test specimen over a wide range of frequencies and temperatures would be particularly useful for material characterization and routine quality control applications. This chapter describes the development of such a technique which we call Dynamic Dielectric Analysis (DDA). The term "dynamic" refers to a continuous scanning over a wide frequency range, typically 50 Hz - 10 MHz, and is a major feature of this technique. The speed of data acquisition and the range of frequencies and temperatures that can be studied in a single experiment by DDA, are far beyond the capabilities of conventional bridge methods mentioned above.

II. Experimental

Techniques

The technique of DDA, developed in the present study uses network analysis techniques to obtain the equivalent passive network components of the test sample. Figure 2.1 shows a block diagram of the experimental set-up and the data analysis path. A Hewlett-Packard Model 3320B fre-

(a)

(b)

Figure 2.1(a): A block diagram of the experimental set-up for DDA

(b): Data analysis path in DDA

quency synthesizer provides a sinusoidal signal which is applied both to the sample and the reference channel of the network analyzer. A Hewlett-Packard Model 3570A network analyzer measures the attenuation and phase shift due to the test sample. The network analyzer has a frequency range extending from 50 Hz to 13 MHz. From the attenuation (G) and phase shift (ϕ), an equivalent network is obtained for the test sample. This is shown in Figure 2.2. The resulting network equations are derived in Appendix 2.A. The dielectric parameters represented by the relative dielectric constant ϵ' , ϵ'' , loss tangent, $\tan \delta$, and resistivity ρ are obtained from the equivalent network and the sample geometry as summarized in Table 2.1. A Hewlett-Packard 9825 desk top computer system is used to record gain and phase (G/ϕ) information and for remote control of the frequency synthesizer and network analyzer.

The sample holder arrangement for DDA is a conventional parallel-plate configuration with silver electrodes and lead wires. Measurements are carried out on disc-shaped specimens.

III. Procedure

The sample is first loaded in the test-cell, care being taken to insure proper loading of the electrode plates on the sample surfaces. The electrodes are then connected to the frequency synthesizer and network analyzer through high-impedance FET probes. The network analysis system is readied for operation by loading the control programs from floppy disc into the 9825 memory. The number of frequency points to be scanned in each decade is pre-selected by the control program. A complete frequency spectrum of the G/ϕ values; a typical scan time for covering the frequency range 50 Hz - 10^7 Hz being one minute. The opera-

a - FET - PROBE GAIN

Z_p - FET - PROBE IMPEDANCE

Z_s - SAMPLE IMPEDANCE

V_s - SYNTHESIZER OUTPUT VOLTAGE

V_A - NETWORK ANALYSER INPUT-A VOLTAGE

V_B - NETWORK ANALYSER INPUT-B VOLTAGE

Figure 2.2: Equivalent network of the test-sample for DDA

Table 2.1: Equations relating ϵ' , ϵ'' , $\tan \delta$ and ρ to sample RC components from network analysis.

$$\epsilon' = C_s \frac{d}{A}$$

$$\epsilon'' = \frac{\sigma}{\omega}$$

$$\tan \delta = \frac{\epsilon''}{\epsilon'}$$

$$\rho = \frac{AR_s}{d}$$

A = area of sample surface; d = sample thickness; ω = operating frequency; σ = conductivity of sample; C_s = sample capacitance and R_s = sample resistance.

tor can examine the G/ϕ data being processed by displaying the results on a CRT terminal or other output devices. G/ϕ results from each individual frequency scan are recorded on floppy discs. Data is organized into files on these discs for reduction by automatic analysis programs.

IV. Data Acquisition and Processing

Data acquisition for DDA is completely automated; computer programs* have been developed in this laboratory for conversion of raw experimental G/ϕ data to dielectric parameters that can be directly correlated with work previously reported in the literature. The parameters ϵ' , ϵ'' , $\tan \delta$ and ρ as functions of frequency are either printed out on a line-printer or plotted on a Hewlett-Packard Model 9872 digital plotter.

V. Error Analysis and Data Reproducibility

Errors inherent in DDA measurements are mainly instrumental.

The performance of the test set-up for DDA was checked with standard capacitor and resistor components combined in parallel. Table 2.2 summarizes the range of values in ϵ' , ϵ'' , ρ , and $\tan \delta$ that is usually measured and the associated errors in their measurement. A more detailed analysis of the measurement network is reported elsewhere (19). Stray capacitance effects were automatically accounted for in the experimental results from "dummy" measurements carried out with air-gap between the electrodes. Good electrical contact between the sample surface and the electrodes was ensured by appropriate loading of the electrode contact plates. Silver paint was employed in a few experiments to reduce contact resistance but subsequent investigation proved this effect to be negligible. Electrode effects were checked by comparing results of measurements with

* All programs are written in HPL language. Copies of control and data analysis programs are available from the authors on request.

Table 2.2: Range of $\tan \delta$ values and errors in the measurement of ϵ' , ϵ'' , $\tan \delta$ and ρ due to the network analyzer^a for midband frequency, 10kHz.

Sample $\tan \delta$	$\pm\%$ Error ϵ'	$\pm\%$ Error ϵ''	$\pm\%$ Error $\tan \delta$	$\pm\%$ Error ρ
300	100	1.5	100	1.5
30	15	1.3	18.0	1.3
3.0	1.5	1.0	3.0	1.0
0.3	0.5	1.0	1.5	1.0
0.03	0.4	5.0	6.0	5.0

^a Using gain linearity ± 0.01 dB near 0 dB and phase linearity $\pm 0.02^\circ$ near 0° .

different electrode materials; no noticeable effect was found. Subsequent measurements were carried out with electrodes and lead wires made of silver.

Calibration

Calibration of DDA was carried out with samples of alkali halides. Values obtained for ϵ' and $\tan \delta$ were in good agreement with results reported in the literature (20). Typical calibration results are shown in Table 2.3.

Table 2.3

Typical Calibration Results for DDA

Material	Frequency range	Measured ϵ'/ϵ_0	Reported ^a ϵ'/ϵ_0 (Ref. 14)
NaCl	$10^2 - 10^5$	5.90 ± 0.05	5.90
KCl	$10^2 - 10^5$	4.84 ± 0.10	4.84
KBr	$10^2 - 10^6$	4.94 ± 0.05	4.90

^aThe nominal accuracies reported for the ϵ'/ϵ_0 values of the various materials in Ref. 14 are $\pm 2\%$.

APPENDIX 2.A

The FET Probe gain $a \equiv a(s)$ is slightly frequency dependent, and its effect is effectively cancelled by using two probes into the network analyzer to determine the complex gain:

$$\frac{V_2}{V_1} = \frac{a(s)V_B}{a(s)V_A} = \bar{G}$$

The gain is calculated from the voltage-divider expression (ignoring source resistance):

$$\bar{G} = \frac{Z_p}{Z_p + Z_s} \quad (1)$$

Solving for Z_s gives:

$$Z_s = Z_p \frac{1 - \bar{G}}{\bar{G}} \quad (2)$$

which in polar form is:

$$|Z_s| \equiv \kappa = \frac{|Z_p| \cdot |1 - \bar{G}|}{|\bar{G}|} \quad (3)$$

$$\angle Z_s \equiv \phi = \angle Z_p + \angle(1 - \bar{G}) - \angle \bar{G} \quad (4)$$

The right-hand side values must be determined.

$\angle \bar{G}$ and $|\bar{G}|$ in dB are found directly from the network analyzer.

$$|1 - \bar{G}| = \sqrt{1 - 2A \cos \theta + A^2} \quad (5)$$

$$\angle(1 - \bar{G}) = -\tan^{-1} \left(\frac{\sin \theta}{\frac{1}{A} - \cos \theta} \right) \quad (6)$$

where $A \equiv |\bar{G}|$, $\theta \equiv \angle \bar{G}$.

The FET-Probe input impedance Z_p can be modeled as a parallel resistance and capacitance:

$$|Z_p| = \frac{R_p}{1 + (\omega R_p C_p)^2} \quad (7)$$

$$\angle Z_p = -\tan^{-1}(\omega R_p C_p) \quad (8)$$

where R_p is the input resistance and C_p is the input capacitance and ω is the angular frequency: $\omega = 2\pi f$.

The equivalent resistance and capacitance of the sample (R_s, C_s) can be determined from equations (3) and (4) by the relations:

$$R_s = \kappa \sec \phi$$

$$C_s = -\frac{1}{\omega \kappa} \sin \phi$$

DYNAMIC DIELECTRIC ANALYSIS OF CATALYST POWDERS

I. Introduction

Various types of sample holders were tested for the dielectric measurements on powdered samples, with a view to:

- (a) Compare the dielectric behavior of γ -irradiated catalyst materials and unirradiated control samples with a view to gain insight on the effect of γ -irradiation on the catalytic properties, and
- (b) Correlate the observed trends in the dielectric behavior with the effectiveness of the material as a radiation catalyst.

Monitoring of the dielectric parameters was carried out by the Dynamic Dielectric Analysis (DDA) technique described in the previous Chapter 2. The various steps in the development of a technique for powders are summarized below:

II. Experimental

Sample Holder:

A considerable amount of trial and error was necessary to attain a satisfactory test set-up for the dielectric measurements on powders. It was found that a coaxial electrode arrangement gave the best results (Figure 3.1). In this configuration the sample is packed fairly tightly (using a tamping rod) in the cavity between the two electrodes. The resistance R and capacitance C values corresponding to the sample are obtained from the gain and phase information using the DDA technique. From the sample geometry, it is then possible to calculate the dielectric parameters viz., dielectric constant, ϵ' , dielectric loss ϵ'' and loss tangent, ϵ''/ϵ' of the sample using well-known equations (see also Appendix 2.A).

Figure 3.1: Sample holder for dielectric analysis of catalyst powders.

III. Procedure

Stray capacitance (arising from electrode leads; etc.) and fringing fields are taken into account by a "sample-in" and "sample-out" measurement (18). Calculation of the theoretical empty air capacitance of the sample cell and comparison with experimental values also yield the magnitude of the combined stray and fringing capacitance values (for example, see Table 3.1).

The next step in the analysis is the correction of the obtained dielectric parameters (corresponding to powders) to values representing the bulk crystals. A search of the literature on this topic yielded equations relating ϵ' and ϵ'' for powders with those for the bulk crystals. These are enumerated below:

(a) Böttcher's formula (21):

$$\frac{\epsilon_p - 1}{3\epsilon_p} = \frac{\delta(\epsilon_s - 1)}{\epsilon_s + 2\epsilon_p} \quad (1)$$

where ϵ_s is the electrical permittivity of the material in bulk and ϵ_p is the permittivity of the powder sample at packing fraction δ .

The packing fraction δ is an important variable, it is defined as the ratio of the density of the powder to that of the bulk crystals. Equation (1) can be modified for dielectric loss correlation if ϵ_s and ϵ_p are replaced by the complex quantities $\epsilon'_s - i\epsilon''_s$ and $\epsilon'_p - i\epsilon''_p$. We then obtain the following equations for the dielectric constant ϵ'_s and dielectric loss ϵ''_s :

$$\epsilon'_s = \frac{(2\epsilon'_p - 3\delta - 2)\{(\epsilon'_p)^2 + (\epsilon''_p)^2 + \epsilon'_p\} - 2\epsilon''_p^2}{(3\delta - 1)^2 (\epsilon'_p)^2 + (\epsilon''_p)^2 + 2\epsilon'_p(3\delta - 1) + 1} \quad (2)$$

Table 3.1: Comparison of Calculated and Experimental
Open Air Cell Capacitance¹

Frequency (Hz)	Capacitance (pF)					
	Measured			Calculated ⁵		
	C_p^2	C_o^3	C_T^4	C_p	C_o	C_T
100	4.28	6.81	11.09	4.01	8.03	12.04
1,000	3.93	7.93	11.86	3.68	8.03	11.71
10,000	3.72	7.91	11.63	3.48	8.03	11.51
100,000	3.48	8.02	11.50	3.35	8.03	11.38
1,000,000	3.41	8.34	11.75	3.26	8.03	11.29

¹ The difference between calculated and measured C_T is attributed to stray and fringing capacitance effects.

² Contribution from Plexiglass plug.

³ Open air capacitance.

⁴ Total capacitance.

⁵ Calculated from the formula $C = \frac{2\pi\epsilon_o \ell}{\ln(b/a)}$

where ϵ_o = free space permittivity i.e., 8.86×10^{-14} F/cm

ℓ = length of the electrodes (7.696 cm)

a = inner electrode radius (0.798 cm)

b = outer electrode radius (1.270 cm)

$$\epsilon_s'' = \frac{2(3\delta - 1) (\epsilon_p''^3 + \epsilon_p'^2 \epsilon_p'') + \epsilon_p''(3\delta - 2) + 4\epsilon_p' \epsilon_p''}{(3\delta - 1)^2 (\epsilon_p'^2 + \epsilon_p''^2) + 2\epsilon_p'(3\delta - 1) + 1} \quad (3)$$

Equation (2) for loss-loss case ($\epsilon'' = 0$, $\epsilon' = \epsilon$) reduces to

$$\epsilon_s = \frac{\epsilon_p (2\epsilon_p + 3\delta - 2)}{(3\delta - 1) \epsilon_p + 1} \quad (4)$$

For most of the materials examined in the current program (viz., oxides in the unreduced state), the above approximation is valid and we can use Eq. (4).

(b) Landau-Lifshitz-Looyenga's formula (22,23):

$$\epsilon_p^{1/3} - 1 = \delta (\epsilon_s^{1/3} - 1) \quad (5)$$

$$\epsilon_s'' = \frac{\epsilon_p''}{\delta} \left(\frac{\epsilon_s'}{\epsilon_p'} \right)^{2/3} \text{ for } \epsilon''/\epsilon' \ll 1 \text{ (which is the usual case in practice)} \quad (6)$$

Correlation of the dielectric constants ($\epsilon'' \approx 0$ for all the materials studied thus far) for the powders with those for bulk crystals was attempted using Eqs. (4) and (5). A comparison of the results obtained from the two equations is shown in Table 3.2. The packing factors for these calculations were obtained from an experimental determination of the densities of the powders and from corresponding data in the literature for the single crystals.

IV. Calibration

The test set-up described above and shown in Figure 3.1 was calibrated using NaCl, MgO and TiO₂. Typical calibration results are shown in Table 3.3. Sample computer data output sheets are included in Appendix 3.A.

Table 3.2: Correlation of Dielectric Constants for Powders with Those For Bulk Crystals Using Böttcher's Formula and Landau-Lifshitz-Looyenga Equation

Frequency (Hz)	MgO ¹			TiO ₂ ¹			NaCl ¹		
	ϵ_p	$\epsilon_s(1)^2$	$\epsilon_s(2)^3$	ϵ_p	$\epsilon_s(1)$	$\epsilon_s(2)$	ϵ_p	$\epsilon_s(1)$	$\epsilon_s(2)$
100	1.528	12.58	--	5.649	95.20	--	--	--	--
1,000	1.434	9.46	20.68	3.163	30.86	--	--	--	--
10,000	1.367	7.52	14.36	2.592	19.85	89.74	4.92	8.16	8.20
100,000	1.361	7.36	13.62	2.440	17.20	52.92	3.17	4.96	4.84
1,000,000	1.347	6.99	12.08	2.402	16.56	47.20	2.99	4.59	4.49

¹ Packing factors 0.115, 0.219 and 0.665, respectively for MgO, TiO₂ and NaCl.

² $\epsilon_s(1)$ obtained from Landau-Lifshitz-Looyenga equation (Eq. 5 in the text).

³ $\epsilon_s(2)$ calculated from Böttcher's formula (Eq. 6 in the text).

Table 3.3: Typical Calibration Results for NaCl, MgO and TiO₂

Frequency (Hz)	NaCl		MgO		TiO ₂	
	C ¹ (pF)	R ² (ohm)	C (pF)	R (ohm)	C (pF)	R (ohm)
100	--	--	10.41	1.51×10^{13}	38.47	1.22×10^{11}
1,000	--	--	15.13	1.97×10^{12}	25.07	8.41×10^{10}
10,000	39.12	3.69×10^{13}	14.59	5.93×10^{12}	24.32	--
50,000	28.93	1.18×10^{13}	14.50	4.19×10^{12}	23.39	--
100,000	25.45	7.40×10^{12}	14.40	5.57×10^{12}	23.06	--
500,000	24.33	2.10×10^{12}	14.44	--	23.01	--
1,000,000	24.93	1.49×10^{12}	14.69	--	--	--

¹ Capacitance values corrected for fringing and stray values.

² The high resistance values validate approximation ($\epsilon'' \approx 0$) mentioned in the text.

V. Comments on the Performance of DDA for Powders

The key to a satisfactory performance of the test set-up lies in:

- (a) Minimizing stray capacitance and fringing effects. This can be done by increasing the total empty air capacitance of the sample holder by reducing electrode separation and increasing length of sample cell; in this situation, the interfering capacitance effects become only a small fraction of the total measured capacitance, thus increasing measurement accuracy. Trial and error methods and theoretical calculations were used to arrive at suitable dimensions for the sample cell.
- (b) Increasing the packing factor, δ by suitable compression of the powder compact. Equations (4) and (5) are extremely sensitive functions of δ especially at low packing levels.
- (c) The dielectric parameters are extremely sensitive to moisture. Thorough drying of the samples is necessary for the dielectric measurements. The oxides are pre-calcined at $\sim 800^{\circ}\text{C}$ to remove all traces of water and NaCl is dried at $\sim 110^{\circ}\text{C}$.

VI. Future Work

The proposed future work will consist of comparing the results for the powdered oxide materials with those for the irradiated samples. We plan to study these effects as a function of (a) irradiation time and (b) length of storage. On the basis of prior literature work and intuitively speaking, one would expect significant changes in ϵ'' on γ -irradiation and very little effect on ϵ' .

FREQ.	CAP.	(PF)	RES.
50	14.863	-3.67E	11
63	10.701	2.06E	11
79	7.734	-1.25E	12
100	11.090	-4.16E	11
105	10.243	-4.56E	11
132	11.533	-1.19E	12
166	12.132	-1.47E	12
209	11.897	2.51E	12
263	11.993	3.30E	13
331	12.021	-6.67E	12
417	11.626	-4.76E	13
501	11.938	5.17E	12
631	11.910	5.46E	12
794	11.897	5.17E	12
1000	11.856	5.19E	12
1050	11.856	5.19E	12
1320	11.842	5.13E	12
1660	11.828	5.14E	12
2090	11.801	5.21E	12
2630	11.788	5.27E	12
3310	11.761	5.41E	12
4170	11.747	5.41E	12
5250	11.720	5.49E	12
6610	11.693	5.57E	12
8320	11.680	5.64E	12
10500	11.666	5.71E	12
13200	11.653	5.86E	12
16600	11.639	6.02E	12
20900	11.613	6.11E	12
26300	11.613	6.35E	12
33100	11.586	6.45E	12
41700	11.573	6.73E	12
52500	11.559	7.04E	12
66100	11.533	7.50E	12
83200	11.519	8.28E	12
105000	11.506	9.81E	12
132000	11.506	1.34E	13
166000	11.506	1.41E	13
209000	11.519	2.09E	13
263000	11.480	2.54E	13
331000	11.480	1.61E	14
417000	11.519	-2.00E	13
525000	11.559	-9.39E	13
661000	11.633	-7.09E	12
832000	11.747	-6.93E	12

OPEN AIR

FREQ.	CAP. (Pf)	RES.
50	106.397	1.26E 10
63	36.934	2.62E 10
79	23.683	1.36E 12
100	42.749	1.32E 11
105	34.703	1.92E 11
132	34.908	9.09E 10
166	49.480	3.14E 10
209	38.185	5.51E 10
263	38.013	5.88E 10
331	35.191	6.88E 10
417	33.913	7.62E 10
501	32.653	8.41E 10
631	31.220	9.33E 10
794	29.987	1.14E 11
1000	29.002	1.31E 11
1050	28.836	1.35E 11
1320	27.953	1.56E 11
1660	27.223	1.80E 11
2090	26.664	2.07E 11
2630	26.147	2.37E 11
3310	25.700	2.73E 11
4170	25.347	3.14E 11
5250	24.999	3.58E 11
6610	24.713	4.09E 11
8320	24.487	4.65E 11
10500	24.318	5.30E 11
13200	24.123	5.96E 11
16600	23.984	6.73E 11
20900	23.847	7.56E 11
26300	23.710	8.40E 11
33100	23.601	9.23E 11
41700	23.465	1.02E 12
52500	23.385	1.12E 12
66100	23.250	1.23E 12
83200	23.143	1.39E 12
105000	23.064	1.62E 12
132000	22.941	1.93E 12
166000	22.984	2.27E 12
209000	22.981	2.57E 12
263000	22.852	3.41E 12
331000	22.852	6.21E 12
417000	22.852	4.84E 13
525000	23.041	-1.34E 13
661000	23.170	-6.12E 12
832000	23.433	-5.13E 12

TiO₂

FREQ.	CAP.	(pf)	RES.
50	16.980	-2.01E	12
63	18.194	2.14E	11
79	15.737	3.29E	11
100	14.637	-1.51E	13
105	16.843	3.87E	11
132	16.290	5.38E	11
166	15.450	1.46E	12
209	15.503	1.07E	12
263	15.486	1.20E	12
331	15.450	1.30E	12
417	15.379	1.49E	12
501	15.308	1.60E	12
631	15.256	1.72E	12
794	15.185	1.84E	12
1000	15.133	1.97E	12
1050	15.116	2.00E	12
1320	15.064	2.11E	12
1660	15.012	2.26E	12
2090	14.977	2.38E	12
2630	14.925	2.52E	12
3310	14.891	2.64E	12
4170	14.857	2.76E	12
5250	14.823	2.94E	12
6610	14.772	3.00E	12
8320	14.755	3.13E	12
10500	14.586	5.93E	12
13200	14.687	3.36E	12
16600	14.636	3.47E	12
20900	14.619	3.57E	12
26300	14.586	3.72E	12
33100	14.592	3.84E	12
41700	14.519	4.01E	12
52500	14.502	4.19E	12
66100	14.469	4.43E	12
83200	14.435	4.91E	12
105000	14.402	5.57E	12
132000	14.386	6.87E	12
166000	14.402	7.68E	12
209000	14.386	8.01E	12
263000	14.369	1.20E	13
331000	14.353	2.75E	13
417000	14.369	-3.85E	13
525000	14.435	-1.47E	13
661000	14.535	-9.52E	12
832000	14.637	-9.42E	12

Mgo.

THIN FILM FABRICATION

I. Ion Beam Sputtering

In the sputtering process, positive gas ions (usually argon ions) produced in a glow discharge (gas pressure 20 to 150 μm) dislodge groups of atoms which then pass into the vapor phase and deposit onto the substrate. Several types of high quality oxide layers have been sputter deposited using a neutralized ion beam source. This technique utilizes accelerated ions, generally argon, but differs from other sputtering techniques in that all electric fields and charge separation is contained within the source chamber. The primary sputter beam is neutralized in the sense that it contains equal numbers of ions and electrons.

The basic beam source is a modified Kaufman thruster (24), first developed for spacecraft propulsion. This type of beam has proven useful for high resolution pattern etching, surface texturing, and thin film deposition (25-27). Advantages of using this type of beam for sputter deposition include (1) independent control of all parameters, (2) electrical neutrality at both target and substrate, (3) relatively low energy (80 - 800 eV), collimated beam, (4) ability to sputter insulating targets without special preparation, (5) straightforward in situ cleaning of both target and substrate, (6) relatively low bell jar pressure ($< 10^{-4}$ torr), and (7) ease of reactive sputtering. The drawbacks are (1) the relatively slow deposition rate ($\sim 1\mu/\text{hour}$) and (2) the somewhat complex source required.

II. Deposition

The neutralized ion beam source is shown schematically in Figure 4.1. Accelerated electrons from a hot cathode collide with the source gas producing positive ions. The number of ions produced, which determines the density of sputtered particles, can be varied by adjusting the cathode

Neutralized ion beam sputtering

Figure 4.1: Neutralized ion beam sputtering technique

current. This density is increased by lengthening the effective cathode to anode path for the electrons through an arrangement of permanent magnets with fields the order of 100 gauss. The positive ions are accelerated by a negative voltage on the lower grid. The upper, or screen, grid is positively biased to deflect the ions so they will pass through the holes. Both grids are made of graphite sheet with the holes in hexagonal arrays aligned with one another.

Ions emerging from the source pass by a hot filament which injects sufficient electrons to neutralize the beam. The accelerator grid is kept slightly negative to prevent these electrons from backstreaming into the source. The resulting beam consists of positive ions of energy equal to the anode potential, which can be varied. These particles all have very nearly the same velocity both in magnitude and direction. The neutralizing electrons have much higher velocities, randomly oriented with an average component equal to that of the ions. (see Figure 4.2).

There is a probability, proportional to the residual gas pressure, of the positive ions neutralizing through charge exchange, and a much smaller probability of direct recombination to the ground state. One consequence of the higher electron velocity is that the beam tends to be slightly more negative at the edges than in the center. The beam also tends to dissipate somewhat in both energy and intensity due to collisions with residual gas atoms. By introducing the argon, or other gas, directly into the source chamber, well sealed except for the grid holes, this problem can be minimized.

The arrangement for sputter deposition is shown in Figure 4.3. During start-up the beam is blocked by a shutter. The attached beam current monitor measures the ion current falling on a fixed area when the

Figure 4.2: Schematic of beam

Figure 4.3: Sputter deposition arrangement

monitor is biased to repel electrons. By translating the shutter, it can also be used to measure the beam uniformity. Neutralization is obtained at zero net current when the monitor is at ground potential.

An aperture above the target and substrate constrains the beam cross section to be no greater than the projection of the target in its plane, hence minimizing stray sputtering. Other parts of the fixturing are constructed of materials that will not introduce disastrous impurities in deposited layers if stray sputtering should occur. The target itself can be a metal, insulator, packed powder, or essentially any physically contained, low vapor pressure material.

Pre-deposition sputter etching of the target and substrate is possible. In the configuration pictured, the substrate is rotated first to position A where the beam falls on the target, but the sputtered particles are shielded from the substrate. In position B the substrate is cleaned. This step is much more critical because one wants to avoid surface damage. One procedure to avoid this is to reduce the beam energy to about 100 eV and to etch for above five minutes.

In position C actual sputter deposition takes place. The angles and positions of the target and substrate should be chosen to give reasonably uniform coverage and still keep the substrate out of the beam path. In many cases oxygen or nitrogen is introduced between target and substrate to produce a film chemically different from the target used or to fine tune the stoichiometry of the deposited layer. The substrate holder does contain a heater which in some cases improves the quality of the device being fabricated. (Ambient temperatures during deposition in the absence of such heating are the order of 400°C at the target and 200°C at the substrate).

The ion source used in the fabrication process is a model #2.5-500-10 manufactured by Ion Technology, Inc. of Fort Collins, Colorado. A schematic diagram of the vacuum system used with the source is shown in Figure 3.4.

Figure 4.4: A schematic diagram of the vacuum system

REFERENCES

- (1) Th. Wolkenstein. Effect of small quantities of impurities on the catalytic activity of ionic catalysts, *J. Phys. Chem. USSR* 24, 1068-82 (1950).
- (2) Th. Wolkenstein. The electron theory of catalysis, *Advan. Catal.* 12, 189-264 (1960).
- (3) P. B. Weisz. Electronic barrier layer phenomena in chemisorption and catalysis, *J. Chem. Phys.* 20, 1483-84 (1952).
- (4) O. V. Krylov. "Catalysis by Non-metals," Academic Press, New York (1970).
- (5) F. S. Stone, in "Chemistry of the Solid State (W. E. Garner, ed.), pp. 637-404, Academic Press, New York (1955).
- (6) C. Wagner. The mechanism of the decomposition of nitrous oxide on Zinc oxide as catalyst, *J. Chem. Phys.*, 18, 69-71 (1950).
- (7) C. G. B. Garrett. Quantitative considerations concerning catalysis at a semiconductor surface, *J. Chem. Phys.*, 33, 966-979 (1960).
- (8) F. Garcia-Moliner. The band picture in the electronic theories of chemisorption on semiconductors, *Catal. Rev.* 2, 1-66 (1969).
- (9) H. Chon and C.D. Prater. Hall effect studies of carbon monoxide oxidation over doped Zinc oxide catalysts, *Disc. Faraday Soc.*, 41, 380-393 (1966).
- (10) Akira Fujishima, Koichi Kohayakawa and Kenichi Honda. Hydrogen production under sunlight with an electrochemical cell, *J. Electrochem. Soc.* 122, No. 11, 1487-89 (1975).
- (11) M. S. Wrighton, D. L. Morse, A. B. Ellis, D. S. Ginley, and H. B. Abrahamson. Photoassisted Electrolysis of water by UV irradiation of an Antimony doped stannic oxide electrode, *J. Amer. Chem. Soc.*, 98 (1), 44-48 (1976).
- (12) M. S. Wrighton, A. B. Ellis, P. T. Wolczanski, D. L. Morse, H. B. Abramson, and D. S. Ginley, Strontium titanate photoelectrodes, Efficient photoassisted electrolysis of water at zero applied potential. *J. Amer. Chem. Soc.*, 98(10), 2774-2779 (1976).
- (13) M. S. Wrighton, D. S. Ginley, P. T. Wolczanski, A. B. Ellis, D. L. Morse, and A. Linz. Photoassisted electrolysis of water by irradiation of a titanium dioxide electrode, *Proc. Nat. Acad. Sci, USA*, Vol. 72, No. 4, pp. 1518-1522 (1975).
- (14) J. G. Mavroides, D. I. Tchernev, J. A. Kafalas, and D. F. Kolesar. Photoelectrolysis of water in cells with TiO_2 anodes, *Mat. Res. Bull.* Vol. 10, p. 1023-1030 (1975).

- (15) A. K. Ghosh and H. P. Maruska. Heterogeneous sensitized decomposition of water with sunlight, *NSF RANN Report*, No. PB 258-870 (1976).
- (16) J. B. Birks and J. Hart, editors "Progress in Dielectrics, Volume 3. John Wiley & Sons (1961).
- (17) P. Hedvig, "Dielectric Spectroscopy of Polymers," John Wiley & Sons, (1977).
- (18) N. E. Hill, W. E. Vaughan, A. H. Price and M. Davies, "Dielectric Properties and Molecular Behavior," Chapter 2, p. 108, Van Nostrand-Reinhold (1969).
- (19) R. Nottenburg and M. Freeman. *J. Physics E.*, in press.
- (20) A. Von Hippel, editor "Dielectric Materials and Application," p. 334, Technology Press of MIT and John Wiley & Sons (1954).
- (21) C. J. F. Böttcher, "Theory of Electric Polarization," Elsevier, Amsterdam, (1952). p. 415.
- (22) L. D. Landau and E. M. Lifshitz, "Electrodynamics of Continuous Media," Pergamon Press, London (1960). p. 46.
- (23) H. Looyenga, *Physica*, 31, 401 (1965).
- (24) H. R. Kaufman and P. D. Reader in "Electrostatic Propulsion," D. B. Langmuir, E. Stuhlinger, and J. M. Selen, editors, Academic Press, New York, (1961) p. 3.
- (25) J. B. DuBow, D. E. Burk, and J. R. Sites. *Appl. Phys. Lett.*, 29, (1976) 494.
- (26) L. G. Meiners, R. C. Pan and J. R. Sites. *J. Vac. Sci. Technol.*, 14 (July/August 1977).
- (27) J. R. Sites. *Proc. 7th Intern. Vac. Congr. & 3re Intern. Conf. Solid Surfaces*, Vienna (1977).

ON THE THEORY FOR ELECTROCHEMICAL SOLAR CELLS

S. Kar, Department of Electrical Engineering, Indian Institute of Technology, Kanpur - 208016, India

J. DuBow, P. Singh, and K. Rajeshwar, Department of Electrical Engineering, Colorado State University, Fort Collins, CO 80523, U.S.A.

ABSTRACT

A theoretical analysis of the electrochemical solar cell (ECSC), consisting of an electrolyte sandwiched between the semiconductor and the metal electrodes, has been carried out. The treatment includes barrier formation, electrostatic analysis, cell operation under illumination, electron, hole and ion transport, and equivalent circuits. The aim has been to clarify some points which have not yet been well understood and to explain the operation of the device in the solar cell mode. It is shown that the electrostatic analysis of the ECSC is similar to that of MIS(Metal-Insulator-Semiconductor)/SIS(Semiconductor-Insulator-Semiconductor) solar cells except that the insulator is replaced by the interphase and the electrolyte is equivalent to the metal in MIS or the semiconductor in SIS. One of the main differences between the electrolyte in ECSC and the metal in MISSC (MIS Solar Cell) is that in the electrolyte the current is ionic while in the metal it is electronic. Another is that in a pure electrolyte with one redox couple there is just one electronic state to which electrons/holes can be transferred to while in a metal there is a continuum. For efficient solar cell operation and for high rates of charge transfer across the interphases, the work function of the electrolyte should be nearly identical to the metal work function, as well as to the sum of the semiconductor electron affinity and the semiconductor bandgap in case of n-type semiconductor. Also the concentration of ions in the electrolyte should be high and the

semiconductor surface charge density low. Under these conditions, the light-generated current will be generation limited and no degradation of the semiconductor will take place. In addition there will be no or very few states in the electrolyte for the transfer of majority carriers to take place. This will severely reduce the diode or the leakage current. It should then be possible to obtain an open-circuit voltage close to the flatband voltage and also close to the bandgap of the semiconductor.

1. Introduction

A semiconductor-electrolyte junction is encountered in many important practical applications and situations such as anodic oxidation, electrolysis, and photo-electrochemical cells. Therefore these systems, in general, have been the subject of intensive investigation for a long time [1-3]. For some time, photoelectrolysis [4] and very recently electrochemical solar cells [5-13] have been receiving increasing attention in view of the urgent need to find new but inexpensive sources of energy. The electrochemical solar cell is quite attractive because of the following potential advantages it possesses over the conventional p-n junction, and other solid state solar cells such as MS(Metal-Semiconductor)/MIS/SIS cells: (a) The processing cost is greatly reduced since fabrication is much simpler; i.e. no diffusion, as in case of p-n junction, or barrier metal evaporation, as in case of MS/MIS cells, is required. The junction needed to separate the photon-generated electron-hole pair is formed simply by bringing a semiconductor surface in physical contact with a suitable electrolyte. (b) Since the semiconductor-electrolyte junction gives rise to a surface barrier, there is no dead layer at the surface as in a p-n junction solar cell, and carriers generated in the depletion layer are collected efficiently. The latter is of great advantage in materials with low minority carrier diffusion lengths such as polycrystalline semiconductors. (c) The electrolytes are in general transparent and absorb very little visible light and can also serve as the antireflection coating. (d) Since the semiconductor

does not undergo any high temperature processing, no degradation of the original lifetime takes place. (e) There is a large choice of electrolytes and for each electrolyte the pH can be varied. This permits formation of large surface barriers on any semiconductor irrespective of its electron affinity and bandgap. The range of redox potentials available with different electrolytes is about 6.0 V [14] and for any electrolyte the redox potential can be varied by about 0.83 V at 300°K by varying the pH. In comparison, as in case of MS Schottky barriers, quite often, the barrier height is limited by a small choice in the metal work function. The range of metal work functions generally available is about 2.0 eV [15]. (f) Some semiconductors, such as amorphous silicon and II-VI compound and oxide semiconductors are difficult to obtain in both n- and p-type. In such cases, p-n junction solar cells cannot be fabricated. However this does not limit their use as electrochemical solar cells. (g) Perhaps the greatest advantage of the electrochemical solar cell lies in the fact that very high values of V_{oc} (open circuit voltage)/ E_G (band gap of the semiconductor) can be obtained. This ratio is about 0.5-0.6 for p-n junction solar cells [16]. Some recent experiments indicate values as high as 1.10/1.43 for GaAs [5] and that open-circuit voltage V_{oc} equal to the flat band voltage V_{FB} can be obtained with electrochemical solar cells [5]. This means that the diode current, as encountered in conventional solar cells, is negligible. In an MS Schottky barrier solar cell, the high diode current leads to very poor values of V_{oc} , and the value of V_{oc} is generally about $(0.50 \text{ V} - \phi_n)$ lower than the flat band voltage at 300°K and 1.0 Sun illumination, where, ϕ_n is the difference between the Fermi level and the majority carrier band edge. It seems that by suitable manipulation of the redox

potential, the diode current can be reduced, leading to the realization of very high open-circuit voltages, and therefore, potentially high conversion efficiencies.

In spite of the formidable advantages mentioned above, the electrochemical solar cell may not find widespread application unless the following problems can be solved. (a) The useful lifetime of the cell has been severely limited by degradation of the semiconductor electrode. (b) The stability of the electrolyte under operating conditions remains to be established. (c) In some cases the cell resistance seems to be high. This is most probably due to choice of improper cell geometry or counter-electrode or difficulty in charge transfer at the counterelectrode.

A major contribution to these problems originates from our incomplete understanding of the operation of an electrochemical solar cell [6,8, 17,18]. The semiconductor-electrolyte junction has been studied extensively both theoretically and experimentally, and a large amount of experimental data is available [1-17]. However our physical understanding of this complex system is still only partial, and in case of the electrochemical solar cell, quite meager. Many important questions related to the operation of this type of solar cell remain unresolved. For example, the manner in which a charge makes a complete circuit through the cell, in series with the load, to generate the terminal current has still not been explained. Although the electron or hole transport through the semiconductor is well understood, it is not clear by what mechanism electron/hole transfer takes place across the interphase between the electrode surface and the ion. And if tunneling is involved in this transfer, what defines the tunneling barrier? Secondly, what is the highest open-circuit voltage possible for a given semiconductor, i.e. what is the highest V_{oc}/E_G ratio possible? If the open-circuit voltage can be as high as the

flat-band potential, then the diode current must be negligible, and if so, then what is the mechanism by which the diode current is reduced? Finally what would be the equivalent circuit representation of an electrochemical solar cell, i.e. is it different from the familiar representation of a constant current generator in parallel with a rectifier?

The aim of this paper has been to answer the above questions and thereby add to our present understanding of the electrochemical solar cell. This should help us in solving present problems and perhaps ultimately lead to an optimal design of the cell. Suggestions, moreover, have been made regarding the design of the electrochemical solar cell structure, and also electrical measurements and characterization that will improve our understanding of the device.

2. Electrochemical Solar Cell Structure

A suitable structure for an efficient electrochemical solar cell has yet to be suggested. However, it is critically important that all experiments with electrochemical solar cells be carried out on a structure that is appropriate for conversion of light energy into electrical energy and which bears some resemblance to its future form. To cite an example, in past experiments, all kinds of materials and form have been used for the counterelectrode; such as a platinized platinum or platinum wire, tin oxide deposited on a glass slide, or platinized platinum wire grid. Moreover, many types of cell geometry and cell arrangement, many of them unsuitable and impractical from solar cell and light collection point of view, have been employed, i.e. orientation of the counterelectrode with respect to the active electrode and the distance between them, the manner in which light is shone on the semiconductor electrode, and the type of light source and its intensity. Even the use of a third

reference electrode such as NHE (Normal Hydrogen Electrode) or SCE (Standard Calomel Electrode) in a solar cell configuration complicates the structure and is unnecessary. In ECSC, the potential of the semiconductor electrode should be measured with respect to the counterelectrode, as is always done in all other types of solar cells.

Figure 1(a) contains the sketch of a suggested structure for the electrochemical solar cell panel. The semiconductor electrode can be a polycrystalline wafer or a thin polycrystalline or amorphous layer on a suitable substrate with a back ohmic contact. The counterelectrode is a thin metal grid deposited on glass or on polymer sheet which also becomes the cover for the solar cell. One possible design for the grid is shown in Figure 1(b), however, any other among the various forms used in conventional solar cells can also be employed. An optimal grid design should reduce the resistance at the counterelectrode without exceeding an area coverage of, say, 10%. The grid metal is to be suitably chosen so that it is not expensive, is chemically resistant to the electrolyte, and has a work function not very different from that of the electrolyte. Both the back ohmic contact and the grid can be deposited by vacuum evaporation, electroplating, or silk screen printing. The electrolyte can be sandwiched between the cover and the semiconductor wafer, and can be very thin, i.e. < 1.0 micron, since only a thin layer is needed for creating the semiconductor surface barrier.

3. Formation of Junction Barrier

One of the roles of the electrolyte in an electrochemical solar cell is to produce the surface barrier in the semiconductor electrode so that when photocarriers are generated in it by light, the electrons and holes can be separated to give rise to a light generated current and a photovoltage. To produce a barrier at the semiconductor surface there has to

be an exchange of electrons or holes between the majority carrier band in the semiconductor and the ions in the electrolyte. This is similar to the exchange of electrons/holes at an MS contact before equilibrium is established. There exists an interphase or double layer region between the semiconductor and the electrolyte analogous to the interfacial region between a semiconductor and a metal [19]. This makes the semiconductor-interphase-electrolyte system resemble an MIS or an SIS system; i.e. the interphase replaces the insulator and the electrolyte replaces the semiconductor in SIS or the metal in MIS. Although the electrolyte has often been treated as a metal, it does not bear much resemblance to the latter. In fact, it is more appropriate to compare it to a high bandgap semiconductor, such as indium or tin oxide, which are generally known as transparent conductors. In other words, one can think of the electrolyte as a high bandgap material since it is transparent. Generally, a high bandgap material is insulating. However, in case of transparent conductors such as indium or tin oxide, the high conductivity is due to degeneracy while in an electrolyte the high conductivity is due to the presence of mobile ions. Thus, one of the main differences between indium or tin oxide and an electrolyte will be that in the former conduction is electronic while in the latter it is ionic.

Figure 2 represents the energy band diagram of an electrochemical solar cell whose structure is shown in Figure 1. The device voltage is zero and the semiconductor is n-type. A conduction band and a valence band separated by a large bandgap of the order of 4-6 eV have been pictured for the electrolyte. This model, however, would apply better to a

transparent solid electrolyte than to an aqueous or liquid electrolyte. There are two interphases in the cell, one between the semiconductor and the electrolyte and the other between the metal and the electrolyte. The interphase includes the Helmholtz and the Gouy layers [1-3]. The surface barrier or band-bending in the semiconductor, at zero bias ψ_i^0 , depends on the difference between the work function of the electrolyte ϕ_E and the semiconductor electron affinity χ_s , cf. Figure 2:

$$\psi_i^0 = (\phi_E - \chi_s) / q - \phi_n - \Delta^0. \quad [1]$$

In equation (1), ϕ_n is the difference between the conduction band edge E_c and the Fermi level E_{FS} in bulk semiconductor, and Δ^0 is the potential across the interphase at zero bias. The potential Δ^0 consists of the voltage across the Helmholtz layer Δ_1^0 , and that across the Gouy layer Δ_2^0 . The magnitude of Δ^0 can be significant if the density of surface charges on the semiconductor is large and the interphase region is thick either because of a multilayer adsorption of ions or because of a low ionic concentration in the electrolyte. It can be shown that for high ionic concentrations and a low density of surface charges on the semiconductor, Δ^0 will be a small fraction of the semiconductor band-bending ψ_i^0 .

The hypothetical situation before the electrolyte comes into contact with both the electrodes and before equilibrium is established is illustrated by the energy band diagram of Figure 3. When the electrolyte is in contact with both the electrodes, charge transfer occurs through both the interphases until the Fermi levels in the three layers line up with each other and equilibrium is established. After physical contact is made, electrons will be transferred from the semiconductor conduction

band if the semiconductor work function ϕ_s is less than ϕ_E , and from the electrolyte to the metal if ϕ_E is less than the metal Fermi level, ϕ_M . It is clear from equation (1) and Figures 2 and 3 that to obtain a high surface barrier on n-type semiconductor, the work function of the electrolyte should be much higher than that of the semiconductor, and ϕ_n should be small or the semiconductor doping density N_{doping} should be high. However, very high doping density leads to low minority carrier lifetime, so N_{doping} will have an optimal value for efficient solar cell operation [16].

The work function of an electrolyte is determined by the redox potential. Values of the redox potentials are generally available with respect to the NHE [14], from which ϕ_E can be obtained according to the relation:

$$\phi_E = -q \cdot E^{\circ} + \phi_{\text{NHE}} + kT (\ln C_{\text{ox}} / C_{\text{red}}) \quad [2]$$

E° is the redox potential. The work function of the NHE is generally taken to be 4.50 eV, however, it has been suggested that 4.80 eV may be a more accurate value [8]. C_{ox} is the concentration of the oxidized form and C_{red} is the concentration of the reduced form in the electrolyte. In case of aqueous electrolytes, equation (2) can be expressed as:

$$\phi_E = -q \cdot E^{\circ} + \phi_{\text{NHE}} + (0.059 \text{ eV}) \cdot \text{pH}, \quad [3]$$

at room temperature, i.e. 300°K.

4. Electrostatic Analysis

From the point of view of electrostatics, the semiconductor-interphase-electrolyte system is very similar to the MIS or the SIS diode with a tunneable insulator thickness [20,21]. Therefore the MIS/SIS diode

analysis can be applied to the present problem with a few modifications. Expressions for the space charge density and the space charge capacitance in terms of the semiconductor band-bending ψ_i are readily available in the literature [22] as surface barriers are encountered in a large number of modern electronic devices such as MOS(Metal-Oxide-Semiconductor)/MIS/SIS and MS structures. Usually the semiconductor band-bending is classified into four regimes: accumulation ($n_s > N_D$), depletion ($n_i < n_s < N_D$), weak inversion ($n_i < p_s < N_D$), and strong inversion ($p_s > N_D$) [22]. For n-type semiconductor, N_D is the donor density, n_s , p_s the conduction electron and hole concentrations, respectively, at the surface, and n_i the intrinsic carrier density. However, in case of a tunneable insulating or interphase layer, strong inversion is never obtained, as the minority carriers are drained away from the surface by tunneling to the electrolyte [20,23]. This is in fact a necessary condition for efficient solar cell operation, i.e. the rate of minority carrier removal through the interphase must equal or exceed their rate of arrival at the semiconductor surface [24]. In the absence of strong inversion, the semiconductor space charge density Q_{sc} can be expressed for n-type semiconductor as: [22,25]

$$Q_{sc} = \pm \{2kT\epsilon_s N_D [\exp(u_s) - u_s - 1]\}^{1/2} \quad [4]$$

ϵ_s is the semiconductor permittivity, and $u_s = q\psi_i/kT$ the normalized band-bending. The negative sign applies when ψ_i is positive and vice-versa. The corresponding expression for the space charge capacitance C_{sc} is: [22,20]

$$C_{sc} = |[\exp(u_s) - 1] \{q^2 \epsilon_s N_D / 2kT [\exp(u_s) - u_s - 1]\}^{1/2}|. \quad [5]$$

For different regimes of the surface potential, equations (4) and (5) can be simplified to: [22, 20]

$$Q_{sc} \approx - [2kT \epsilon_s N_D \exp(u_s)]^{1/2} \quad \left. \vphantom{Q_{sc}} \right\} \text{in accumulation,} \quad [6]$$

$$C_{sc} \approx [q^2 \epsilon_s N_D \exp(u_s) / 2kT]^{1/2} \quad [7]$$

$$Q_{sc} \approx 0 \quad \left. \vphantom{Q_{sc}} \right\} \text{at flat band,} \quad [8]$$

$$C_{sc} \approx [q^2 \cdot \epsilon_s \cdot N_D / kT]^{1/2} \quad [9]$$

$$Q_{sc} \approx [2kT \epsilon_s N_D (-u_s - 1)]^{1/2} \quad \left. \vphantom{Q_{sc}} \right\} \text{in depletion and} \quad [10]$$

$$C_{sc} \approx [q N_D \epsilon_s / 2 (\psi_i - kT/q)]^{1/2} \quad \left. \vphantom{C_{sc}} \right\} \text{weak inversion.} \quad [11]$$

The electrochemical solar cell is expected to operate in weak inversion and depletion [24], so equations (10) and (11) will in general apply under illumination.

A part of the interphase region is expected to be charge free [1-3]. This region is usually referred to as the Helmholtz layer. The electric field in this part of the interphase region will be constant leading to the following relationships:

$$C_H = \epsilon_H / t_1, \quad [12]$$

$$\Delta_1 = (Q_{sc} + Q_{is}) t_1 / \epsilon_H, \quad [13]$$

where C_H is the capacitance of this layer, ϵ_H the permittivity, t_1 the thickness, Δ_1 the potential, and Q_{is} the surface state charge density.

In equation (13), Q_{sc} can be neglected unless the semiconductor surface is in accumulation. In depletion or weak inversion, the contribution of Q_{sc} to Δ_1 will be small. For example, assuming $\epsilon_s = 11 \epsilon_o$, $N_D = 1.0 \times 10^{16}/\text{cm}^3$,

$\psi_i = -1.0$ V, $t_1 = 5$ Å, and $\epsilon_H = 6 \epsilon_0$ would result in $Q_{sc} \cdot t_1 / \epsilon_H \approx 5$ mV. However, the contribution from Q_{is} to Δ_1 can be significant if Q_{is} is large. For example, if the total surface state density N_s is $1.0 \times 10^{13} / \text{cm}^2$ and all of them contribute to Q_{is} , then $Q_{is} \cdot t_1 / \epsilon_H$ will be about 150 mV for $t_1 = 5$ Å and $\epsilon_H = 6 \epsilon_0$.

The part of the interphase region, where there is a diffuse layer of ions and the electric field is not constant is generally referred to as the Gouy layer [1-3]. The treatment of the electrostatics of this layer is similar to that of a semiconductor surface except that in the solution of Poisson's equation the space charge density ρ consists of positive and negative ions only, since in a transparent electrolyte there will be very few electrons and holes. Expression for the capacitance of this layer C_G can be found in the literature: [1-3]

$$C_G = [2q^2 z^2 \epsilon_G n_0 / kT]^{1/2} \cdot \cosh (q \cdot z \cdot \Delta_2 / 2kT), \quad [14]$$

where ϵ_G is the permittivity of the layer, z the valence of ions, and n_0 is the concentration of either positive or negative ions in bulk electrolyte. For a given value of $(Q_{sc} + Q_{is})$, the potential Δ_2 across this layer and its thickness can be calculated according to the relations: [1-3]

$$|Q_{is} + Q_{sc}| = |Q_G| = [8 \epsilon_G kT n_0]^{1/2} \cdot |\sinh (q \cdot z \cdot \Delta_2 / 2 kT)|, \quad [15]$$

$$t_2 = \epsilon_G / C_G. \quad [16]$$

In the absence of surface charges and for high concentration of ions in the electrolyte, Δ_2 will have a small value. For example, for 0.01M concentration, $T = 300^\circ\text{K}$, $\epsilon_G = 35 \epsilon_0$, $z = 1$, $N_D = 1.0 \times 10^{16} / \text{cm}^3$, $\psi_i = -1.0$ V, and $Q_{is} = 0$, $\Delta_2 = 3.7$ mV, and $t_2 = 21$ Å. On the other hand,

if $N_s = 10^{13}$ states/cm² and $Q_{is} = q \cdot 10^{13}$ /cm², we obtain $\Delta_2 = 75$ mV, and $t_2 = 9\text{\AA}$.

In summarizing the above discussion, one may conclude that for low density of surface charges, and high ionic concentrations, i.e. $N_s < 10^{12}$ states/cm² and $n_0 > 10^{18}$ /cm³, the potential drop across the interphase $\Delta = \Delta_1 + \Delta_2$ will be small. On the other hand if Q_{is} is significant and/or ionic concentration is low, Δ can be significant leading to a smaller barrier at the semiconductor surface according to equation (1).

The equivalent circuit of the semiconductor-interphase-electrolyte system in dark and at 300°K can be represented by the diagram in Figure 4(a). C_{sc} is the space charge capacitance given by equation (5). C_{inv} is the inversion layer capacitance and in the case of an efficient solar cell should be negligible. R_s is the series resistance whose main sources are the bulk semiconductor and the back ohmic contact. R_I is the resistance resulting from the transfer of minority carriers across the interphase, and R_D is associated with their transport across the neutral region in the semiconductor. R_O is the resistance associated with the transfer of majority carriers across the interphase. In dark, the value of R_D is high, and for efficient solar cell operation, R_O should be very high. The equivalent circuit in Figure 4(a) strongly resembles that for an MIS/SIS structure with a tunneable insulator [20, 22, 26]. The high and low frequency limits for the circuit in Figure 4(a) are shown in Figure 4(b) and Figure 4(c) respectively [20,22,26]. The ac signal frequency is considered high when the surface states and the minority carriers cannot follow it [22]. In dark and at 300°K it is about 1 MHz [22]. And the frequency is considered low when all the states as well as the minority carriers can follow it. This is about or less than 1 Hz

[22, 27]. The total high and low frequency capacities of the semiconductor-interphase-electrolyte system can be expressed, respectively, as:

$$1/C_{HF} = 1/C_G + 1/C_H + 1/C_{sc}, \quad [17]$$

$$1/C_{LF} = 1/C_G + 1/C_H + 1/(C_{sc} + C_{is}), \quad [18]$$

$$C_{is} = q \cdot N_{is}, \quad [19]$$

where N_{is} is the number of states /eV / cm².

In a tunnel MIS diode, the surface states can communicate with majority carriers or minority carriers in bulk semiconductor or with the metal. However unless the electrolyte has a large variety of impurity ions, communication of surface states with the electrolyte will, in the case of most states, be negligible because the electrolyte will not have states for the electrons/holes in the surface states to tunnel to. Therefore the surface states will in general communicate with the majority carriers in dark as the rate of minority carrier supply to the surface is very low [26]. However under light, communication of minority carriers with the surface states will improve [22, 24]. This means that the majority carrier quasi-Fermi level will determine the surface state occupancy in dark [26, 20]. In such a case, the capacitance-voltage and the conductance-voltage characteristic of the device will exhibit strong frequency dispersion as observed in case of MOS structures [20, 22, 23, 26], and it should be possible to obtain the surface state density distribution using the capacitance and the conductance techniques [20, 26, 27, 28].

For high ionic concentration, the capacitance C_G is going to be

larger than C_H . In such a case, the device capacitance will tend to saturate in strong accumulation as happens in the case of MOS structures [20,22], cf. Figure 4. The saturated device capacitance can be equated to C_H and the thickness of the Helmholtz layer could be obtained from it according to equation (12). To obtain a feeling for the relative magnitudes of C_G and C_H let us assume: $\epsilon_G = 35 \epsilon_o$, $\epsilon_H = 6 \epsilon_o$, $n_o = 6 \times 10^{20}/\text{cm}^3$, $T = 300^\circ\text{K}$, $Q_{is} = 0$, $N_D = 1.0 \times 10^{16}/\text{cm}^3$, $\psi_i = -1.0 \text{ V}$, and $t_1 = 5 \text{ \AA}$. Then $C_G = 1.5 \times 10^{-4} \text{ F/cm}^2$ and $C_H = 1.06 \times 10^{-5} \text{ F/cm}^2$. The high frequency capacitance for reverse as well as low forward bias can be approximated to C_{sc} , cf. Figure 4(b), since generally C_{sc} is, in depletion and weak inversion, $\ll C_H$ and C_G for high ionic concentrations. If the surface charge density is also low, and therefore $\partial\Delta/\partial\psi \ll 1.0$, then the $1/C^2$ vs. V characteristic will be a straight line according to the relationships, cf. equation (11):

$$d(1/C^2)/dV = 2/q \cdot N_D \cdot \epsilon_s, \quad [20]$$

$$1/C^2 = 2 (\psi_i^0 - V - kT/q) / q \cdot N_D \cdot \epsilon_s, \quad [21]$$

and its intercept with the V -axis will be equal to $(\psi_i^0 - kT/q)$, from which the zero bias semiconductor barrier ψ_i^0 can be obtained. The semiconductor doping density can be obtained from the slope of the characteristic, cf. equation (20).

The electrochemical cell consists of the semiconductor-interphase-electrolyte and the electrolyte-interphase-metal systems. If $\phi_M \neq \phi_E$, then there will be a potential across the metal-electrolyte interphase and also at the metal surface. For efficient solar cell operation, the metal should be chosen such that $\phi_M \approx \phi_E$; i.e. interphase region will be very thin. In subsequent analysis, it will be assumed that the potential

across the electrolyte-interphase-metal system is small and its capacitance is large. Since this capacitance is in series with the capacitance of the rest of the cell, it can be neglected for obtaining the total device capacitance.

5. Cell under Illumination

The energy band diagram of the electrochemical solar cell under illumination has been presented in Figure 5. It has been assumed that the semiconductor is n-type and the metal work function is so chosen that there is no significant potential across the electrolyte-interphase-metal system i.e. $\phi_M \approx \phi_E$. Photons of energy higher than the semiconductor bandgap generate electron-hole pairs which are separated by the built-in barrier ψ_i at the semiconductor surface, i.e. the electrons go down the band-bending and the holes move up. Flow of minority photo-carriers to the electrolyte gives rise to the light-generated current I_L and also produces the photovoltage V across the electrodes. The photovoltage is always directed in such a manner that the semiconductor band-bending decreases from its value in equilibrium. Under illumination the quasi-Fermi levels for electrons and holes, E_{FS}^e and E_{FS}^h respectively, will be different throughout the semiconductor, i.e. $n.p. \gg n_i^2$, as indicated in Figure 5. For low level injection, the majority carrier quasi-Fermi level remains relatively unchanged up to the surface. The photovoltage V can be expressed in the following manner:

$$V = (\psi_i^0 - \psi_i) + (\Delta^0 - \Delta), \quad [22]$$

which under open-circuit conditions becomes:

$$V_{oc} = (\psi_i^0 - \psi_i^{oc}) + (\Delta^0 - \Delta^{oc}). \quad [23]$$

In an MS solar cell, the value of ψ^{oc} at 300°K under 1.0 Sun illumination is about $(0.5 \text{ V} - \phi_n)$ [24]. This is because of the presence of a diode current I_D which flows in a direction opposite to that of I_L and which increases exponentially with photovoltage [24,22]. The diode current in an MS contact is mainly due to the thermionic emission of majority carriers into the metal [19]. When there is a substantial diode current, then at open-circuit, $I_L = I_D$ [22]. On the other hand, if the diode current is negligible, then at open-circuit, $I_L \rightarrow 0$. In such a case, the open-circuit voltage V_{oc} can approach the value of the flat-band voltage V_{FB} or $(E_G/q - \phi_n)$ whichever is smaller [24,29]. That the open-circuit voltage cannot exceed the flat-band voltage is clear from the fact that if $V > V_{FB}$, then the bands will bend in the opposite direction leading to flow of photocarriers in the wrong direction, i.e. the solar cell cannot operate in the accumulation regime. The flat-band voltage can be expressed as:

$$V_{FB} = (\phi_E - \chi_s) / q - \phi_n - \Delta^{FB}. \quad [24]$$

Equation (24) can be obtained by inspection of the energy band diagram in Figure 6 at flat-band. The situation when V_{FB} exceeds the value of $(E_G / q - \phi_n)$ is illustrated in Figure 6. It is clear that in this case photocurrent suppression will take place because there will be very few photon-generated holes at an energy equal to E_{FL} for transfer to the negative ion in the electrolyte. Open-circuit voltages nearly equal to the flat-band voltage have been measured in electrochemical solar cells [5,30]. Chai and Anderson [5] have obtained an open-circuit voltage of 1.1 V and a flat-band voltage of 1.3 V for an n-type GaAs - 0.1 M HCl-platinized Pt cell at an illumination level of 1.0 mW/cm^2 . The value

of $(E_G/q - \phi_n)$ for their cell would be about 1.36 V.

6. Electron, Hole, and Ion Transport

In conventional solar cells, the current is due to the transport of electrons or holes around the circuit consisting of the cell in series with the load, i.e. the current is electronic. However in an electrochemical solar cell, the current cannot be electronic throughout because there are no mobile holes or electrons in a transparent electrolyte. In an electrolyte, the current is due to the transport of mobile ions. Another significant difference between an electrolyte and a semiconductor or metal is that a pure electrolyte with one redox couple will have only one energy level of high density to which an electron or a hole can be transferred to, from either the semiconductor or the metal. This has been indicated in the energy band diagrams of Figures 5 and 6.

Figure 7 indicates how a charge makes the complete circuit around an electrochemical solar cell and a load in series. The charge flow in the semiconductor is partly due to electron transport and partly due to hole transport, while in the metal it is due to electron transport. In the electrolyte, it is due to ion transport and through the interphase it is due to electron or hole transfer. It is clear that whichever among the mechanisms in Figure 7 has the lowest rate of charge flow will determine the current. For a solar cell, the ideal situation is when the pair generation in the semiconductor is the limiting mechanism. The rate of pair generation increases with light intensity. However in an electrochemical solar cell with high ionic concentrations, the limiting mechanism, in general, tends to be the charge transfer across the interphase [1-3]. If that is the case, photocurrent suppression will take place.

The mechanism for charge transfer across the interphase is believed

to be tunneling [1-3]. Tunneling generally takes place from a filled state to an empty one at the same energy level. Inelastic tunneling is possible but the rates will be much lower. Therefore, for high rates of charge transfer across the metal-electrolyte interphase, it is necessary that the energy level of the ion be located near the metal Fermi level, i.e. $\phi_E \approx \phi_M$, and for the same across the semiconductor-electrolyte interphase be located near the minority carrier band edge of the semiconductor, i.e. $\phi_E \approx (\chi_S + E_G)$, cf. Figure 3. If the energy level of the ion is situated near the minority carrier band edge, and the electrolyte is pure and contains only one redox couple, then there will be no states in the electrolyte for the majority carriers to tunnel to, cf. Figure 5. As a result, the majority carrier diode current will be severely charge transfer limited, will be negligible, and will not have the strong voltage dependence as in case of an MS contact. In case of an MS or MIS solar cell, there is a continuum of states in the metal for the majority carriers to be transported to [19, 22, 31].

In the solar cell mode, the charge flow around the circuit should be in the following manner, cf. Figures 5 and 6: Photons of energy higher than the semiconductor bandgap create electron-hole pairs. The electrons go down the bandbending towards the back ohmic contact and return through the load to the metal counter-electrode and are then transferred to the oxidized form of the redox couple, and a negative ion is produced. The negative ion moves through the electrolyte to the semiconductor-electrolyte interphase and the photon-generated hole, which has moved up the semiconductor band-bending up to the surface, is transferred across the interphase to it. This process gives rise to the light-generated current I_L and in the ideal case should be optical generation rate limited. In such a case,

as the minority carrier is transferred to the ion as soon as it arrives, and no chemical reaction, i.e. oxidation or decomposition can take place on the semiconductor.

Theoretical treatment of the photocarrier transport in the semiconductor would be exactly the same as in case of an MS, MOS, MIS, or SIS solar cell and can be found in the literature [21,22,32,33]. The transport of ions through the electrolyte takes place by diffusion, drift, and convection [1-3] and, in general, is not the limiting rate if the ion concentration is high. The least understood mechanism is the charge transfer across the interphase [1-3,17,34]. Although tunneling is believed to be the mechanism, it is not clear what defines the tunneling barrier. In case of a solid electrolyte, it will be defined by the conduction band edge of the electrolyte and the energy level from which tunneling is taking place, cf. Figure 8. The charge transfer current can be expressed as:

[1-3]

$$I_T = k \cdot T_T \cdot n \cdot p_s = k \cdot T_T \cdot p_s \cdot n_o \cdot \exp(q\Delta_2/kT), \quad [25]$$

where k is a constant, T_T the tunneling transmission coefficient, and p_s the density of photocarriers at the semiconductor surface. The tunneling transmission factor T_T , for a rectangular barrier can be expressed as:

$$T_T \approx \exp - (\phi^{1/2} \cdot t_1), \quad [26]$$

if the barrier height ϕ , cf. Figure 8, is expressed in eV and t_1 in Å. It is clear from equations (25) and (26) that high ionic concentrations and low surface charges would lead to a higher value for the charge transfer rate.

When the ion energy level is located a little bit away from the minority carrier band edge as shown in Figure 8, then inelastic tunneling

is possible; however, a more likely mechanism for minority carrier transfer would be recombination-tunneling via interface states. The recombination time τ_R can be expressed as: [20, 22]

$$\tau_R = 1 / (v_{th} \cdot \tau_h \cdot p_s), \quad [27]$$

where v_{th} is the thermal velocity, and τ_h the capture cross-section of the state for holes.

Figure 9 shows the equivalent circuit of the electrochemical solar cell. R_{dc} represents the shunt resistance through which some leakage current flows. In the case of a conventional solar cell, the leakage current is the diode current and a rectifier replaces R_{dc} . However in ECSC, the majority carrier current will be severely charge transfer limited and is unlikely to exhibit any rectifying characteristics. So it may be more suitable to represent this current flow by the shunt resistance R_{dc} .

7. Conclusions

In summarizing the above discussion, one may conclude that for efficient solar cell operation, the light generated current should be generation limited and not limited by charge transfer across the interphase or ion transport in the electrolyte. To obtain high rates for ion transport, the ion concentration should be high. To obtain a high rate of photo-carrier transfer across the interphases, it is necessary to have $\phi_E \approx \phi_M \approx (E_G + \chi_s)$ when the semiconductor is n-type. Also the surface charge density should be low. Under these conditions, the photon-generated hole will be removed from the surface to the ion as soon as it arrives, and no anodic oxidation will take place. Secondly, a high surface barrier, $\psi_i^0 \approx (E_G/q - \phi_n)$, will result, leading to a high open circuit voltage. Thirdly, if the electrolyte is highly pure, few electronic states will

exist in the electrolyte for majority carrier transfer from the semiconductor, resulting in a very small diode current, which will not have strong voltage dependence. Consequently open-circuit voltages close to the flat-band voltage and close to the semiconductor bandgap can be obtained. The ideal semiconductor bandgap for operation under sunlight will be in the 1.4-1.6 eV range.

Various electrical measurements will be very useful in characterizing the electrochemical solar cell and for understanding its operation. These include capacitance-voltage and conductance-voltage measurements at various frequencies in the range of 40 Hz-1 MHz, and current-voltage measurements under different levels of illumination and at different temperatures. The surface state density and capture cross-section of states can be obtained from the frequency dispersion of C-V and G-V characteristics. The thickness of the Helmholtz layer can be obtained from the saturated capacitance in strong accumulation. The semiconductor doping density and the semiconductor band-bending at zero bias can be obtained from the high frequency (1.0 MHz) $1/C^2 - V$ characteristic. From the I-V characteristic of the cell, fill factor, conversion efficiency, and the series resistance can be obtained. From the variation of the short-circuit current and the open-circuit voltage with the light intensity and the temperature, one could obtain an indication of the limiting mechanism for the current.

REFERENCES

1. V. A. Myamlin and Y. V. Pleskov, *Electrochemistry of Semiconductors*, Plenum Press (New York, 1967).
2. H. Gerischer in "Physical Chemistry," Vol. IXA, Edited by H. Eyring, D. Henderson and W. Jost, Academic Press (New York, 1970).
3. J. O. M. Bockris and A. K. N. Reddy, *Modern Electrochemistry*, Plenum Press (New York, 1970).
4. K. Rajeshwar, P. Singh and J. DuBow, *Electrochim. Acta*, in press. See also references cited therein.
5. Y. G. Chai and W. W. Anderson, *Appl. Phys. Lett.* 27, 183 (1975).
6. R. Williams, *J. Vac. Sci. Technol.* 13, 12 (1976).
7. H. Gerischer and J. Gobrecht, *Berichte der Bunsen - Gesellschaft* 80, 327 (1976).
8. H. Reiss, *J. Electrochem. Soc.* 125, 937 (1978).
9. J. Manassen, D. Cahen, G. Hodes, and A. Sofer, *Nature* 263, 97 (1976).
10. T. S. Jayadevaiah, *Appl. Phys. Lett.* 25, 399 (1974).
11. M. D. Archer, *J. Appl. Electrochem.* 5, 17 (1975).
12. M. Robbins, K. J. Bachmann, V. G. Lambrecht, F. A. Thiel, J. Thomson Jr., R. G. Vadimsky, S. Menezes, A. Heller, and B. Miller, *J. Electrochem. Soc.* 125, 831 (1978).
13. H. Gerischer, *J. Electroanal. Chem.*, 58, 263 (1975).
14. W. M. Latimer, *Oxidation Potentials*, Prentice Hall (New York, 1952).
15. S. Kar, *Solid-St. Electron.*, 18, 169 (1975).
16. M. Wolf, *Energy Conversion* 11, 63 (1971).
17. H. Gerischer, *J. Electrochem. Soc.* 125, 218 C (1978).
18. R. H. Wilson, *J. Appl. Phys.*, 68, 4292 (1977).
19. E. H. Rhoderick, *Metal Semiconductor Contacts*, Oxford University Press, (Oxford, 1978).
20. S. Kar and W. E. Dahlke, *Solid-St. Electron.* 15, 221 (1972).
21. J. Shewchun, J. DuBow, A. Myszkowski, and R. Singh, *J. Appl. Phys.* 49, 855 (1978).

22. S. M. Sze, *Physics of Semiconductor Devices*, Wiley and Sons (New York, 1969).
23. S. Kar, *IEDM Technical Digest*, 79 (1976).
24. S. Kar, *J. Appl. Phys.* 49, August, 1978.
25. S. Kar and W. E. Dahlke, *Solid-St. Electron.*, 15, 869 (1972).
26. E. H. Nicollian and A. Goetzberger, *Bell Syst. Tech. J.* 46, 1055 (1967).
27. C. N. Berglund, *IEEE Trans. Electron Devices* ED-13, 701 (1966).
28. M. Kuhn, *Solid-St. Electron* 13, 873 (1970).
29. S. Kar, *IEDM Technical Digest*, 56A (1977).
30. J. H. Kennedy and K. W. Frese, *J. Electrochem. Soc.* 125, 723 (1978).
31. S. Kar, D. Shanker, S. P. Joshi, and S. Bhattacharya, *Conf. Record of the 13th IEEE Photov. Spec. Conf.*, Washington, D.C. (1978).
32. R. F. McQuat and D. L. Pulfrey, *J. Appl. Phys.* 47, 2113 (1976).
33. D. L. Pulfrey, *Photovoltaic Power Generation*, Van Nostrand (New York, 1978).
34. D. K. Roe, *Anal. Chem.* 50, 9R (1978).

FIGURE CAPTIONS

- Fig. 1 Suggested structure for the electrochemical solar cell. The semiconductor electrode can be a polycrystalline wafer or a thin polycrystalline or amorphous layer on a suitable substrate.
- Fig. 2 Energy band diagram of an electrochemical solar cell in dark and at zero voltage for n-type semiconductor.
- Fig. 3 Energy band diagram of the n-type semiconductor, the electrolyte, and the metal before physical contact and equilibrium.
- Fig. 4 (a) Equivalent circuit for the electrochemical solar cell in dark.
(b) Reduction of the circuit in (a) at high frequency, for negligible R_s .
(c) Reduction of the circuit in (a) at low frequency, for negligible R_s .
- Fig. 5 Energy band diagram of an electrochemical solar cell under illumination with n-type semiconductor. It has been assumed that $\phi_M \approx \phi_E$.
- Fig. 6 Energy band diagram of an electrochemical solar cell under illumination with n-type semiconductor at flat band condition. It has been assumed that $\phi_M \approx \phi_E$.
- Fig. 7 Diagram showing the flow of charge around a circuit consisting of an electrochemical solar cell in series with a load.

Fig. 8 Energy band diagram of the semiconductor-interphase system illustrating the tunneling barrier and also charge transfer by recombination-tunneling via interface states.

Fig. 9 Equivalent circuit for an efficient electrochemical solar cell.

(b)