

Lawrence Berkeley National Laboratory

Recent Work

Title

THE CHARACTERIZATION OF p-TYPE AND n-TYPE DOPED IRON OXIDE ELECTRODES FOR THE PHOTODISSOCIATION OF WATER. LOCATIONS OF BAND EDGES, OXYGEN DETECTION, AND LONG TERM STABILITY

Permalink

<https://escholarship.org/uc/item/9r78s3v6>

Author

Turner, J.E.

Publication Date

1983-07-01



Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

Materials & Molecular Research Division

RECEIVED
LAWRENCE
BERKELEY LABORATORY

SEP 26 1983

LIBRARY AND
DOCUMENTS SECTION

Submitted to the Journal of the Electrochemical
Society

THE CHARACTERIZATION OF p-TYPE AND n-TYPE DOPED
IRON OXIDE ELECTRODES FOR THE PHOTODISSOCIATION OF
WATER. LOCATIONS OF BAND EDGES, OXYGEN DETECTION,
AND LONG TERM STABILITY

J.E. Turner, M. Hendewerk, D. Neiman,
and G.A. Somorjai

July 1983

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy
which may be borrowed for two weeks.
For a personal retention copy, call
Tech. Info. Division, Ext. 6782.*



LBL-16411
c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal 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 its 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, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

THE CHARACTERIZATION OF p-TYPE AND n-TYPE DOPED IRON OXIDE ELECTRODES FOR
THE PHOTODISSOCIATION OF WATER. LOCATIONS OF BAND EDGES, OXYGEN DETECTION,
AND LONG TERM STABILITY.

J.E. Turner, M. Hendewerk, D. Neiman, and G.A. Somorjai

Materials and Molecular Research Division,
Lawrence Berkeley Laboratory and
Department of Chemistry
University of California
Berkeley, California 94720, USA

THE CHARACTERIZATION OF p-TYPE AND n-TYPE DOPED IRON OXIDE ELECTRODES FOR
THE PHOTODISSOCIATION OF WATER. LOCATIONS OF BAND EDGES, OXYGEN DETECTION,
AND LONG TERM STABILITY.

J.E. Turner, M. Hendewerk, D. Neiman, and G.A. Somorjai

Materials and Molecular Research Division,
Lawrence Berkeley Laboratory
and
Department of Chemistry,
University of California, Berkeley, CA 94720 USA

ABSTRACT

Band edge locations for both p-type and n-type iron oxide semiconductors in a sodium hydroxide aqueous solution are determined from differential capacitance measurements. The thermodynamic feasibility of the catalytic photodissociation of water without external potential is demonstrated for a short-circuited p/n diode assembly on an energy level diagram depicting the electrode/electrolyte interfaces. The photooxidation of water at the n-type anode has been verified. Oxygen evolution is monitored from an operating diode assembly using mass spectrometry and isotopically labelled water (H_2^{18}O). Photocurrents from these photochemical cells show excellent long term stability and Auger analysis of the semiconductor surfaces indicate no evidence of electrode dissolution.

INTRODUCTION

The photoelectrochemical generation of hydrogen and oxygen from water in semiconductor based systems has been achieved in two different cell configurations. One uses a metal cathode, usually platinum, a semiconductor anode with only the anode illuminated, and an external bias (1). The other employs two semiconductor electrodes, (2,3) a p-type cathode for hydrogen production and an n-type anode for oxygen production, with both electrodes illuminated by light of bandgap or higher energy. The Mg-doped p-type iron oxide/Si-doped n-type iron oxide photochemical diode as described by recent reports from our laboratory (2) belongs to the second group.

Iron oxide satisfies most of the requirements for an ideal solar energy converting material. It has a band gap of 2.3eV (4) which allows 40% of incident solar radiation to be utilized. It also exhibits excellent stability in acidic and alkaline electrolyte solutions. Most attractively, it has been shown that in a short circuited configuration, a Mg-doped p-type iron oxide cathode with a Si-doped n-type iron oxide anode can photodissociate water with no applied external bias (2).

In this work a more complete characterization of the Mg-doped and Si-doped iron oxide electrodes is described. In addition, we present advances in the

operation and stability of the p/n diode assembly. Depletion layer capacitance measurements have been used to determine the flatband potentials and band edge locations for the n- and p-type iron oxide electrodes. A detailed energy level diagram is presented to support the feasibility of water dissociation using an iron oxide p/n diode assembly with no external applied potential.

Oxygen gas production from an isotopically labelled water (H_2^{18}O) solution has been monitored by means of mass spectrometry. Detection of $^{34}\text{O}_2$ confirms that the catalytic oxidation of water occurs at the n-type iron oxide photoanode.

Extended studies of measured photocurrents with time obtained from an operating p/n diode assembly have shown that an induction period of approximately 80 hours occurs in which the photocurrent steadily rises before reaching a plateau of $15\mu\text{A}$. Integration and stability of the photocurrents after more than 360 hours of operation emphasizes that electrode dissolution does not occur.

EXPERIMENTAL

I. Preparation of Doped Iron Oxide Electrodes.

The procedure for preparing p-type and n-type doped iron oxide electrodes has been presented in detail previously (2). Mixing powders of MgO or SiO_2 with $\alpha\text{-Fe}_2\text{O}_3$ results, respectively, in a p-type or n-type doped iron oxide semiconductor. These mixed powders are pressed, sintered, and rapidly cooled in water. Finally, the doped iron oxide discs are mounted on a conductive backing of silver epoxy.

All experiments in the work presented here have been performed with a 10 atomic percent Si doped iron oxide anode and/or a doped iron oxide cathode containing 5 atomic percent Mg.

II. Depletion Layer Capacitance Measurements.

Capacitances of the semiconductor space charge layer, C_{sc} , were independently determined as a function of applied voltage for both the p-type and n-type electrodes. The electrode configuration consisted of a standard three electrode electrochemical cell containing a mercury oxide reference electrode, a platinum counter electrode, and a doped iron oxide anode or cathode immersed in a 0.01 N NaOH solution. An AC voltage with a frequency of $f = 1.5$ kHz was superposed on the DC voltage applied to the working electrode from a Pine RDE potentiostat. Tests were performed under illumination of 35mW/cm^2 intensity focused from a tungsten halogen lamp. Depletion layer capacitances were extracted from the phase shift of the AC current out relative to the AC voltage in by use of a PAR Model 124A lock-in amplifier.

III. Detection of Water Oxidation Products from a p/n Diode Assembly.

A schematic diagram of the apparatus is shown in Figure 1. It consists of a stainless steel cell equipped with two quartz windows permitting simultaneous illumination of both iron oxide electrodes. Light of approximately 5mW/cm^2 intensity was focused with quartz optics and passed through a 5cm water filter to absorb IR radiation before entering the cell. A 0.01N NaOH/H₂O solution containing 6% isotopically enriched

H_2^{18}O (Alpha Ventron Distributors) was used as the electrolyte solution. Gases produced from the water dissociation process were circulated with a small mechanical pump in a closed stainless steel loop containing Ar carrier gas which passed above the electrolyte solution. Gas samples were extracted from the loop at 24 hour intervals and injected into an UHV chamber for mass spectral analysis.

RESULTS

I. Differential capacitance measurements. Mott-Schottky plots and energy level diagram for the p/n iron oxide photochemical diode.

Previously, we reported the successful photodissociation of water in an unbiased p/n diode assembly consisting of doped iron oxides (2). In this assembly, a Mg-doped (p-type) electrode and a Si-doped (n-type) iron oxide electrode acted as a photocathode and photoanode, respectively, for the reduction and oxidation of water. The spontaneous occurrence of these two processes under illumination is thermodynamically feasible only with the proper positioning of the conduction and valence band edges with respect to the redox couples in the electrolyte solution. The reduction of hydronium ions to hydrogen molecules is mediated by electrons from the conduction band of the photocathode. Therefore, a necessary condition for hydrogen production is that the conduction band edge of the Mg-doped iron oxide must lie at a potential more negative than the hydrogen redox couple. Concomitantly, electron vacancies oxidizing hydroxyl ions move spontaneously toward lower potentials. Thus, for water oxidation to occur, the valence band edge for the n-type semiconductor must be more positive

than the standard potential for water oxidation (1.23V, RHE). Locations of the band edges for the Mg-doped and Si-doped iron oxide electrodes were determined in order to check that these criteria were satisfied in our iron oxide based system.

Differential capacitances of the semiconductor space charge layer (C_{sc}) with applied potential (V_a) were measured independently for both the p- and n-type electrodes. Following the Mott-Schottky relation (5, 6).

$$1/C_{sc}^2 = 2(q\epsilon\epsilon_0 A^2 N)^{-1}(V_a - V_{fb}) \quad [1]$$

flatband potentials (V_{fb}) were extracted from the intercept on a plot of the reciprocal capacitance squared ($1/C_{sc}^2$) against applied voltage (V_a).

The Mott-Schottky plots for a 5 atomic percent Mg-doped and a 10 atomic percent Si-doped iron oxide electrode are shown in Figure 2. Voltages are given relative to a reversible hydrogen electrode so that the hydrogen redox couple remains at 0V, RHE and the oxygen redox couple at 1.23V, RHE independent of the pH of the electrolyte solution. From the Mott-Schottky plots of Figure 2 the flatband potentials for the n-type and p-type electrodes are 200mV and 2300mV(RHE) respectively. With these values and the bandgap of α -Fe₂O₃ (2.3eV) (4) band edge locations can be designated on an energy level diagram as shown in Figure 3. For heavily doped semiconductors, the fermi level is nearly coincident with the band containing the majority charge carriers. Thus, in the n-type semiconductor the flatband potential designates the location of the conduction band

edge ($E_{cb} \approx E_{fb} = 200\text{mV, RHE}$). This places the valence band edge of the n-type electrode at 2500mV, RHE , so that the photoproduction of oxygen is easily accomplished. More notable is the coincidence of the conduction band edge of the Mg-doped iron oxide electrode with the hydrogen half cell reaction potential. Equating the valence band edge to the flatband potential ($E_{vb} \approx E_{fb} = 2300\text{mV, RHE}$) and subsequently subtracting the band gap energy (2.3eV) places the conduction band edge at 0V, RHE . With this result it is evident that an illuminated and short circuited p/n diode assembly can photodissociate water to form hydrogen and oxygen gases without applying an external bias.

In addition to values of the flatband potential, donor or acceptor concentrations, N , can be obtained from the Mott-Schottky plots of Figure 2. The slope of the linear region in which relation [1] is obeyed is given by $S = 2(q\epsilon\epsilon_0 A^2 N)^{-1}$ where q is the charge on an electron, ϵ_0 is permittivity of free space, ϵ is the dielectric constant for the sample, A is the electrode area, and N is the donor or acceptor concentration. Surfaces of the doped iron oxides have an area roughness factor of approximately 10 as measured in a krypton-helium BET apparatus (7) (Quantasorb Surface Area Analyzer, Quantachrome Corp.). From the value of $A = 6\text{cm}^2$ for the area and the dielectric constant for pure $\alpha\text{-Fe}_2\text{O}_3$ ($\epsilon = 100$) (8) the acceptor or donor concentrations are $N_A = 5 \times 10^{16}\text{cm}^{-3}$ for the Mg-doped samples and $N_D = 2 \times 10^{18}\text{cm}^{-3}$ for the Si-doped electrodes. Due to uncertainties in the dielectric constants for the doped iron oxides and in surface area determinations, carrier densities are correct only to within an order of magnitude.

II. Oxygen detection during the photodissociation of water in a p/n diode assembly.

Previously, hydrogen was detected by gas chromatography from an illuminated unbiased iron oxide p/n diode assembly. Predicted hydrogen production from integrated photocurrents correlated well with detected amounts of hydrogen gas. With the confirmation of the band edge locations shown in Figure 3 and the previous detection of hydrogen gas, it follows that the measurement of stoichiometric amounts of oxygen from the assembly would be the next important investigation. Detection of oxygen by gas chromatography was not possible due to the presence of additional sources of oxygen, both dissolved in the electrolyte solution and entering the closed loop system through very small leaks. However, the use of isotopically labelled water (H_2^{18}O) and a mass spectrometer has permitted the detection of photoproduct oxygen as $^{34}\text{O}_2$. Initial analysis of the gases in the closed loop system showed no measureable traces of $^{34}\text{O}_2$. Oxygen production was initiated by closing the circuit between the two electrodes and halted by opening the circuit. Figure 4 shows the $^{34}\text{O}_2$ partial pressure as a function of time for a p/n assembly giving an average photocurrent of $2\mu\text{A}$. Constant illumination was provided to prevent variations in solution temperature and spurious gas production from outgassing. As seen in Figure 4, the $^{34}\text{O}_2$ partial pressure increased during those periods in which the circuit was closed and current was flowing. During the open circuit intervals the concentration of $^{34}\text{O}_2$ decreased slightly and then remained constant, as expected. The short

delay in the observable onset of $^{34}\text{O}_2$ production results from the time needed for oxygen in the solution to equilibrate with the gas phase above the solution.

Due to leaks from the system, a direct comparison of oxygen production and integrated photocurrents was not possible. Instead, correspondence between oxygen yield and photocurrent was determined by the ratio $^{34}\text{O}_2/^{32}\text{O}_2$. Calculation of the relative oxygen ($^{34}\text{O}_2$ and $^{32}\text{O}_2$) yields involved two assumptions. Firstly, no spontaneous water dissociation occurs, so that the oxygen initially dissolved in the $\text{NaOH}/\text{H}_2^{18}\text{O}/\text{H}_2^{16}\text{O}$ solution consists only of $^{32}\text{O}_2$ and no $^{34}\text{O}_2$. Secondly, under equilibrium conditions, the ratio of $^{34}\text{O}_2/^{32}\text{O}_2$ in the gas phase above the electrolyte solution is equal to that in solution. Establishment of this equilibrium was also assumed to be fast as compared to sampling frequency (once every 24 hours). The relative amounts of $^{34}\text{O}_2$ and $^{32}\text{O}_2$ that are expected to be produced depend on the relative probabilities of $^{16}\text{OH}^-$ and $^{18}\text{OH}^-$ oxidation at the anode. From a solution containing 6% isotopically labelled H_2^{18}O the detectable concentrations of oxygen isotopes present at any time (t) are

$$[^{32}\text{O}_2] = C_0 + 0.88 \text{ rt} \quad [^{34}\text{O}_2] = 0.12 \text{ rt}$$

where r is the rate of oxygen production. The concentration of $^{32}\text{O}_2$ initially saturating the solution, C_0 , was calculated from Henry's Law to be 4×10^{18} molecules per 15 ml H_2O . With these calculations, the observed total oxygen production showed good correspondence (within 20%) with the predicted value. After the 340 hours of intermittent gas production the predicted value for the ratio of $^{34}\text{O}_2/^{32}\text{O}_2$ was 0.059. The measured value was $^{34}\text{O}_2/^{32}\text{O}_2 = 0.047$.

III. Long term stability of the p/n iron oxide photochemical diodes.

Other important factors governing the viability of technological development of an iron oxide p/n diode assembly for solar energy conversion is the long term stability of the system and the catalytic nature of the photodissociation process. In the past, we found that the photocurrents for our iron oxide based p/n assemblies would gradually decline over an 8 hour period until finally reaching zero. The iron oxide electrodes were regenerated by purging the electrolyte solution with pure oxygen gas. Auger analysis of the electrode surfaces revealed large amounts of carbon present, possibly originating from organic contaminants in the electrochemical cell or other parts of the system. Recently, in a separate experiment, a p/n diode assembly was illuminated in solution while the photocurrent from the production of H_2 and O_2 gases was monitored as a function of time. While an all glass cell was used as in previous experiments, the use of stopcock grease was eliminated. Conductive leads to the electrodes were isolated by silicon rubber sealant from the electrolyte solution prepared with doubly distilled water (specific resistance greater than $2 \times 10^6 \Omega \text{cm}^{-1}$) as in all other experiments reported here. The results of this electrode stability test are shown in Figure 5. At first exposure to the solution a photocurrent of $3 \mu\text{A}$ was measured. During the succeeding 80 hours the photocurrent steadily increased until it reached its maximum value of $15 \mu\text{A}$. Dark currents throughout the test were $< 0.01 \mu\text{A}$. The p/n assembly was continuously illuminated for another 240 hours during which time

a steady photocurrent of $15\mu\text{A}$ persisted. No visible corrosion of the electrodes was detected. 320 hours of operation of a p/n diode assembly producing $10\mu\text{A}$ of current would result in the dissolution of approximately one tenth of the electrode if the doped iron oxide electrodes were being reduced. Comparison of the surface compositions of the electrodes with Auger electron spectroscopy before and after extended operation showed no change, supporting the conclusion that photocurrents are not a result of electrode degradation.

Integration of the observed photocurrents over the 320 hour duration of the stability experiment suggests that a total of more than 5,000 monolayers of hydrogen and 2,500 monolayers of oxygen were produced. This shows that the photodissociation of water by Mg- and Si-doped iron oxides is indeed catalytic.

DISCUSSION

The results of the Mott-Schottky capacitance curves yield an energy level diagram for the p/n diode assembly that indicates that both hydrogen and oxygen can be produced from water without an external potential when the semiconductor electrodes are doped in the proper manner. The shift of the conduction band edge of the p-type iron oxide by 200mV as compared to the n-type electrode can be attributed to the effect of introducing Mg ions into the iron oxide lattice. Butler and Ginley (9) have proposed a model in which the electron affinity of a composite system can be calculated using the geometric mean of the electron affinities of the

constituent atoms. Thus, substitution of Mg dopant atoms ($EA = 1.2\text{eV}$) with an electron affinity less than that of the silicon atoms ($EA = 1.8\text{eV}$) in the iron oxide lattice lowers the effective electron affinity of the semiconductor and shifts the band edges toward more cathodic potentials. Doping with Si on the other hand only enhances the intrinsic n-type character of the iron oxide (1) since the electron affinities are very similar (EA of Fe = 1.7eV).

Comparison of the acceptor and donor densities of the p-type and n-type electrodes shows that the effective doping level of the p-type material leads to carrier concentrations two orders of magnitude less than in the n-type material. Consideration of the acceptor density of the p-type electrode and the effect of shifting the conduction band edge to more favorable cathodic potentials suggests that additional doping might further improve the conditions for hydrogen reduction at the p-type cathode in a p/n diode assembly.

Furthermore, homogeneous acceptor and donor distributions in both the p-type and n-type semiconductors may produce samples with more consistent photocurrents in a p/n diode assembly. Observed curvatures in the Mott-Schottky plots shown in Figure 2 may be due to inhomogeneous dopant concentration (10), particularly for the p-type electrodes. Since p-type Mg-doped electrodes are a new aspect of the iron oxide system, sample preparation has not been perfected. For the p-type electrodes

with 5 atom percent Mg doping only about 0.002 percent of the Mg ions enter the iron oxide lattice substitutionally. The vast majority of the Mg probably remains in its original oxide form (MgO). Similar calculations for the n-type electrodes show that only 0.05 percent of the Si contributes to donor levels. Scanning Auger microscopy has shown that much of the silicon aggregates in silicon rich precipitates, particularly at the surface (2). Thus, it might be beneficial to explore alternative methods of incorporating ions into the iron oxide lattice other than sintering at high temperatures.

As described earlier, differential capacitance measurements indicate the potential for the fermi level under flatband conditions and in turn the location of the band edges of the semiconductors. The operating potential of the illuminated p/n diode assembly was measured separately against a HgO reference electrode. From this the degree of band bending can be obtained. As shown in Figure 3 the fermi level of the operating p/n assembly lies near 750mV,RHE. This same figure shows that the band bending near the surface of the n-type iron oxide is about 550mV, while at the p-type iron oxide surface the bending is greater than 1500mV.

With charge carrier concentrations from the Mott-Schottky plots and the band bending values (V_{BB}) from Figure 3, depletion layer widths can also be calculated. With $W_D = (2\epsilon\epsilon_0 V_{BB}/qN)^{1/2}$ the depletion layer widths in an operating p/n assembly for the n-type and p-type electrodes are approximately 500Å and 5,000Å respectively. These results are

tabulated in Table I along with a summary of the flatband potentials, charge carrier concentrations, and band edge locations for our Mg-doped and Si-doped iron oxide electrodes.

The stability of Mg- and Si-doped iron oxide electrodes is substantiated by both the oxygen detection experiment and the long term stability tests. Detection of $^{34}\text{O}_2$ production verifies that the oxidation of water is occurring at the n-type iron oxide electrode and correlation of the total oxygen production with integrated photocurrents strongly refutes electrode dissolution as a possible source of observed photocurrents or gas production.

The 80 hour induction period described in the stability experiment is perhaps a result of a slow alteration of the surface states on the electrodes. ESCA studies are being conducted to probe the possibility of the formation of hydroxylated intermediates or the oxidation of near surface layers as possible explanations. Attempts to simulate the proposed oxidation process proved unsuccessful. Heating the doped iron oxide electrodes to 50-150°C in a flowing oxygen atmosphere for 6 hours dramatically improved the conductivity of the samples but had little effect on the photocurrent. A transient negative photocurrent was observed for a short period of time in a p/n assembly after both electrodes were heated in an oxidizing atmosphere suggesting that the oxygen treatment was being reversed on at least one of the electrode surfaces. Heating the samples in water vapor did decrease the induction period of the assemblies, but did not affect the final value obtained for the photocurrent of a given p/n assembly.

The sintered and doped iron oxide photoelectrochemical diode assembly at present has a low conversion efficiency ($\eta \approx 0.05\%$) for solar energy to H_2 and O_2 . Uniformity of doping, control of the surface composition and surface states, the possible use of catalysts to accelerate atom recombination, and more desirable electrode configurations (thin films, single crystals) can all improve the degree of power conversion. Calculations using idealized models (see Appendix) indicate that a power conversion efficiency of about 14% may theoretically be attained. Since the p-type iron oxide sample appears to limit photocurrents and photodissociation rates, future work will be directed toward improving the p-type cathode.

ACKNOWLEDGEMENT

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number De-AC03-76SF00098.

APPENDIX

Photoelectrochemical cells for the conversion of solar radiation to chemical are of two types: a semiconductor photoelectrode (usually an n-type anode) coupled with a metal (usually Pt) cathode, or a cell in which both the anode and cathode are illuminated semiconductors. We present theoretical maximum obtainable efficiencies for an iron oxide based system in either configuration. A comparison of efficiencies, obtained as a function of the applied potential difference between the two electrodes shows that a short circuited p/n diode assembly is the more efficient method for producing hydrogen.

Energy level diagrams are presented for both configurations, Figure 6. For the single electrode system, we consider an n-type doped $\alpha\text{-Fe}_2\text{O}_3$ electrode with $V_{fb} = 200\text{mV}$ (RHE) and $E_g = 2.3\text{eV}$. The band edges at the semiconductor/electrolyte interface are assumed to remain fixed. Since the conduction band edge of the n-type electrode lies anodic of the H^+/H_2 redox couple, an applied bias between the metal electrode and the semiconductor of $V_a \geq 0.2\text{V}$ is needed for the photodissociation process to begin. As the potential difference between the two electrodes is increased, the valence and conduction bands will bend in the direction of the arrows as shown in Figures 6a and 6b.

The two semiconductor electrode system shown in Figure 6b considers an n-type $\alpha\text{-Fe}_2\text{O}_3$ electrode against a p-type $\alpha\text{-Fe}_2\text{O}_3$ electrode with flatband potentials of 200mV and 2300mV respectively. For simplicity, we presume equal and opposite band bending on the two electrodes, and assume that the donor and acceptor densities are also equivalent. This yields

This yields identical depletion layer which were chosen to be constant,
 $W_d = 1000\text{\AA}$.

Following arguments from Scaife (11), the total photocurrent from an illuminated semiconductor is

$$J_T = \int_{E_g/h}^{\infty} e\phi(\nu)(1-\exp(-\alpha(\nu)W_dV_{bb}^{1/2})) d\nu$$

where $\phi(\nu)$ is the solar flux at frequency ν (12), $\alpha(\nu)$ is the absorptivity for iron oxide (13), W_d is the depletion layer width, and V_{bb} is the amount of band bending near the semiconductor/electrolyte interface. If the solar energy conversion efficiency is defined as

$$\eta = \frac{\text{Net energy extracted}}{\text{Solar energy input}}$$

then a simple expression for this efficiency when the energy is stored as hydrogen is given by

$$\eta = (1.23 - V_a)J_T/E_T$$

using an integrated solar flux (12) of $E_T = 83\text{mW/cm}^2$. Here we have included a term accounting for energy expended ($-V_aJ_T$) to maintain the external bias.

A comparison of limiting efficiencies for one and two electrode assemblies of iron oxide at various applied potentials is shown in Figure 7. The iron oxide p/n assembly has a potentially greater solar conversion efficiency than the semiconductor/metal electrode system. The p/n assembly has an optimal efficiency of almost 14%, while the best to be expected from the other system is about 5%. Reasons for this are clear. In our idealized model, it is the degree of band bending which determines the ultimate efficiency. The p/n assembly offers substantial band bending of greater than one volt even without applied potential. The n-type iron oxide against a Pt cathode, however, requires considerable bias to achieve the same effect.

While regulating the potential difference between the two electrodes improves the efficiency of the single electrode system up to $V_a = 0.6$ volts, the application of external bias as shown in Figure 7 does not improve the efficiency of the p/n assembly. Band bending is already so large that additional bending provided by the external potential increases the maximum obtainable photocurrent only slightly. In fact, the net efficiency actually decreases due to the energy input required to maintain this potential.

It should be emphasized that efficiencies calculated here are theoretical maxima, and will not likely be attained in operating systems. In practice, other factors including reflection losses, surface and bulk recombination, and surface state effects will reduce these efficiencies. It does appear that in many situations p/n assemblies will offer efficiencies greater than biased semiconductor-metal electrode cells.

REFERENCES

- 1) J.H. Kennedy, R. Shinar, J.P. Ziegler, J. Electrochem. Soc., 127, 2307 (1980).
- 2) C. Leygraf, M. Hendewerk, G.A. Somorjai, J. Catal., 78, 341 (1982)
- 3) A.J. Nozik, Appl. Phys. Lett. 30, 567 (1977).
- 4) Kittel, Introduction to Solid State Physics, J. Wiley and Sons, 1953, p. 276.
- 5) N.F. Mott, Proc. Royal Soc. (London), A171,27 (1939).
- 6) W. Schottky, Z Phys. 113, 367 (1939); 118, 539 (1942).
- 7) S. Lowell, Anal. Chem., 45(8), 1576 (1983).
- 8) S.M. Wilhelm, K.S. Yun, L.W. Ballenger, N. Hackerman, J. Electrochem. Soc., 126, 419(1979).
- 9) M.A. Butler, D.S. Ginley, Chem. Phys. Letters, 47, 319 (1977).
- 10) R. DeGryse, W.P. Gomes, F. Cardon, J. Vermaak, J. Electrochem. Soc. 122, 711 (1975).
- 11) D.E. Scaife, Solar Energy, 21, 41 (1980).
- 12) K.W. Boer, Phys. Status Solidi A, 40, 355 (1977).
- 13) R.C. Vernon, J. Appl. Phys. 33, 2140 (1962).

FIGURE CAPTIONS

Figure 1: Schematic diagram of the apparatus for oxygen detection from an operating p/n diode assembly.

Figure 2: Mott-Schottky plots of the inverse square of space charge capacitance $(1/C_{sc})^2$ versus applied potential (V_a) for n-type and p-type electrodes. Performed at 1.5KHz frequency in 0.01 N NaOH against a Pt counter electrode.

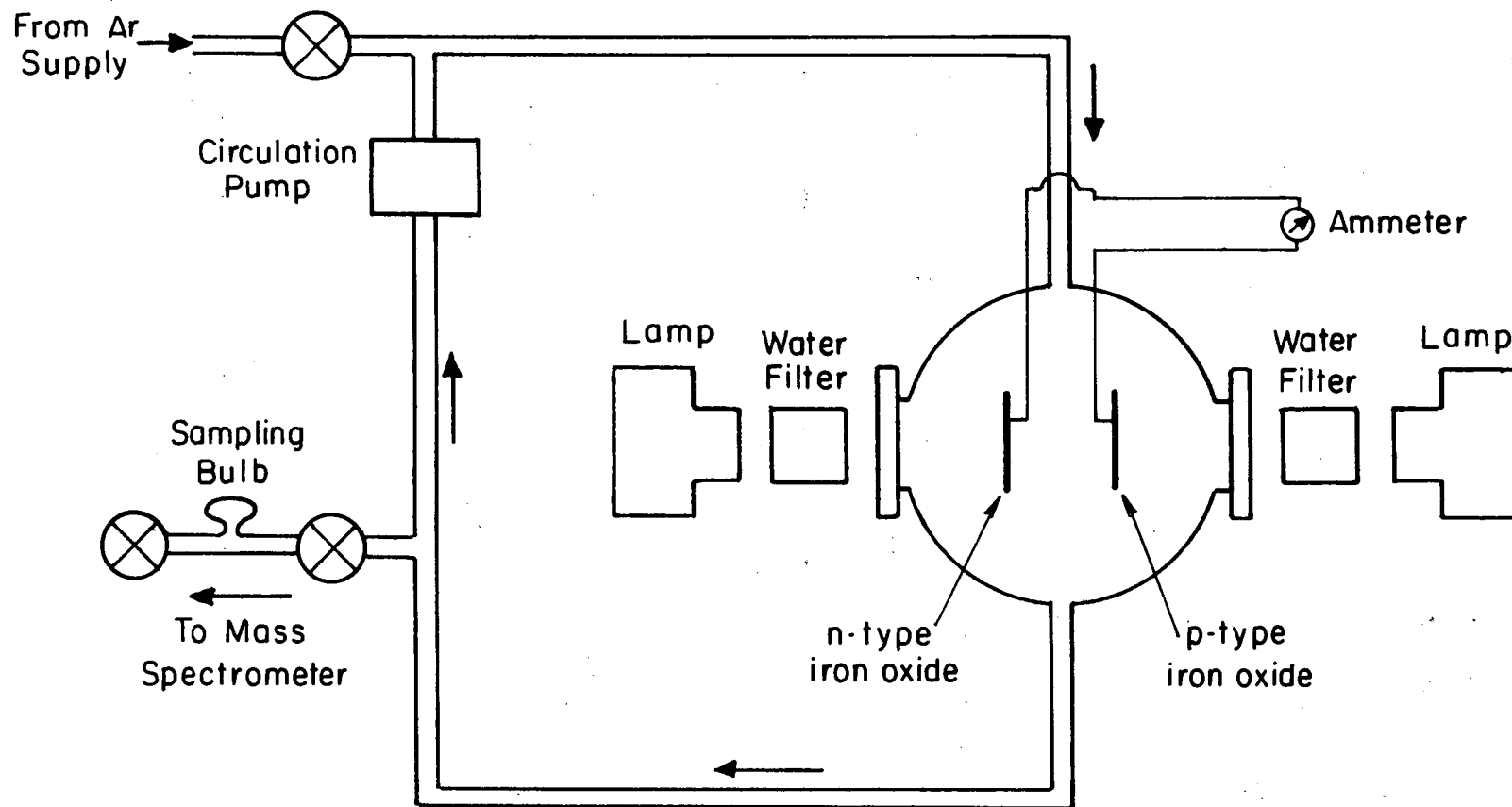
Figure 3: Energy level diagram of the electrode/electrolyte interface for a short circuited p/n assembly.

Figure 4: Oxygen production from an operating p/n assembly. Mass spectrometry was used to monitor $^{34}O_2$ production from water enriched with isotopically labelled $H_2^{18}O$.

Figure 5: Photocurrent stability for the unbiased p/n assembly.

Figure 6: Energy level diagrams for a) a single semiconductor electrode metal electrode system and b) a semiconductor/semiconductor electrode system.

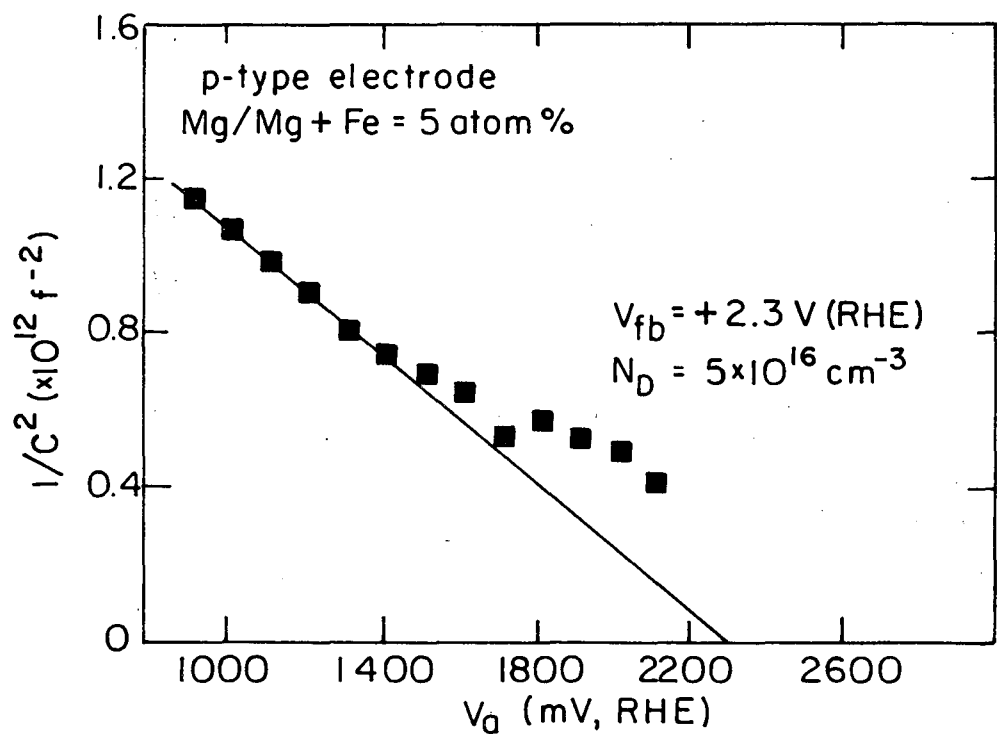
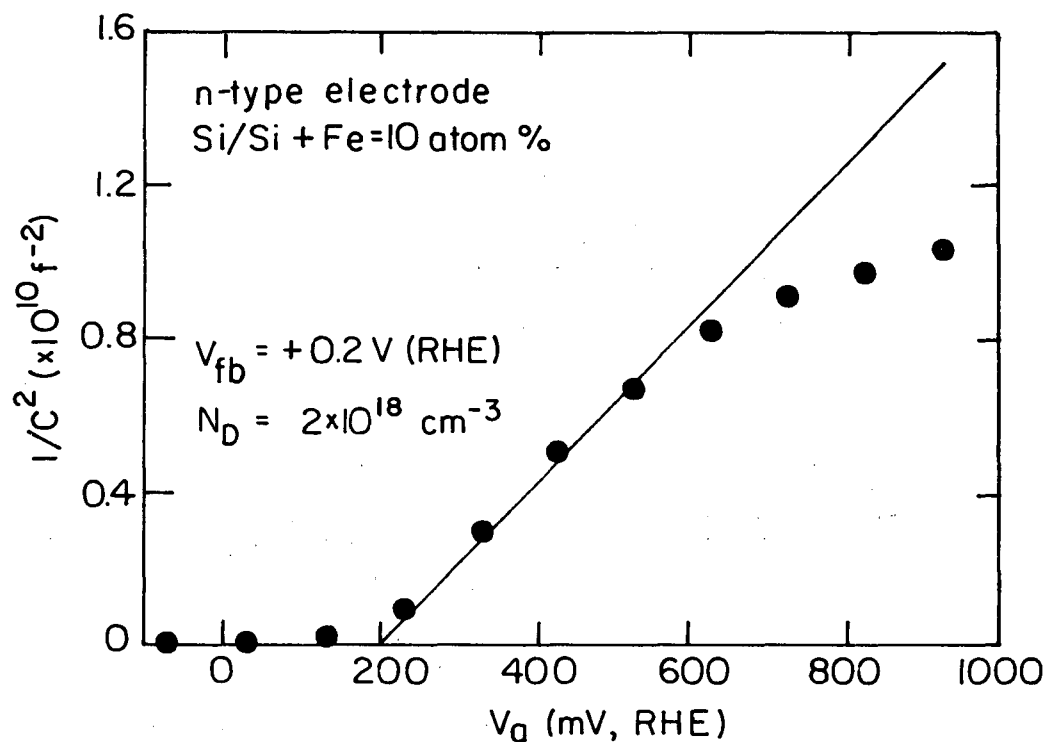
Figure 7: Solar conversion efficiencies as a function of applied potential (V_a) between the electrodes.



-21-

XBL837-6055

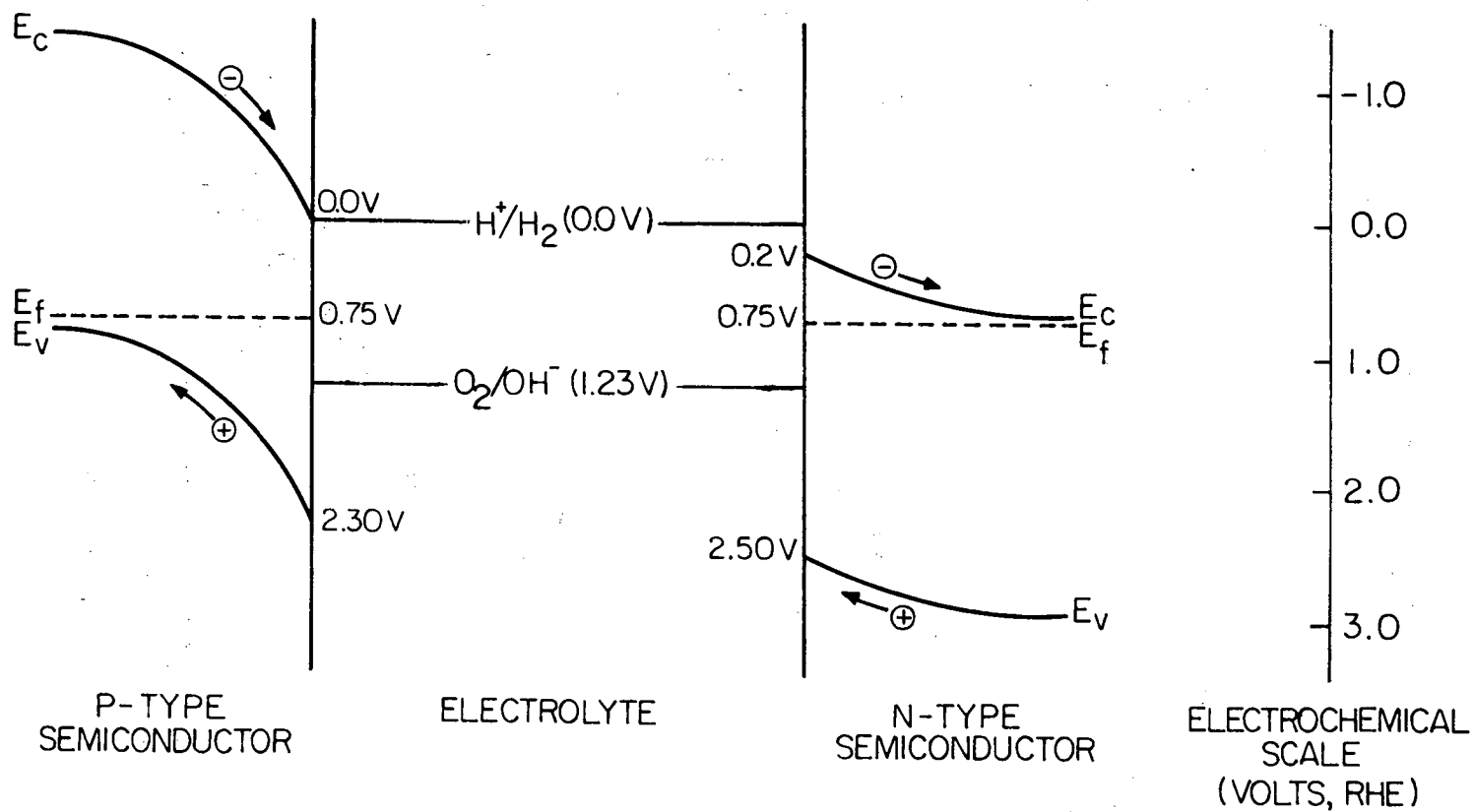
Fig. 1



XBL 831-S155A

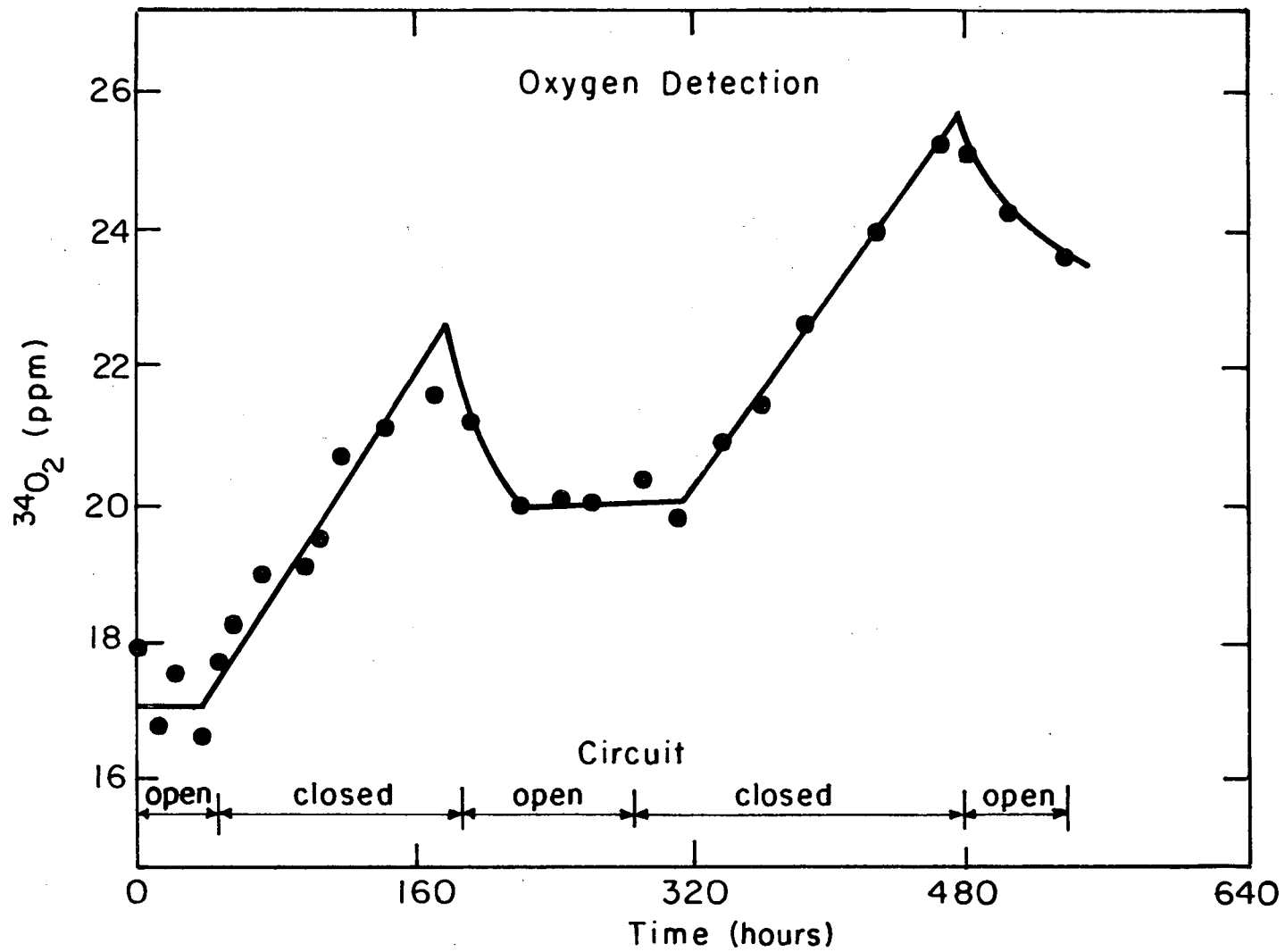
Fig. 2

ENERGETICS OF CONNECTED P-TYPE AND N-TYPE IRON OXIDES



XBL 832-5181A

Fig. 3



XBL835-9804

Fig. 4

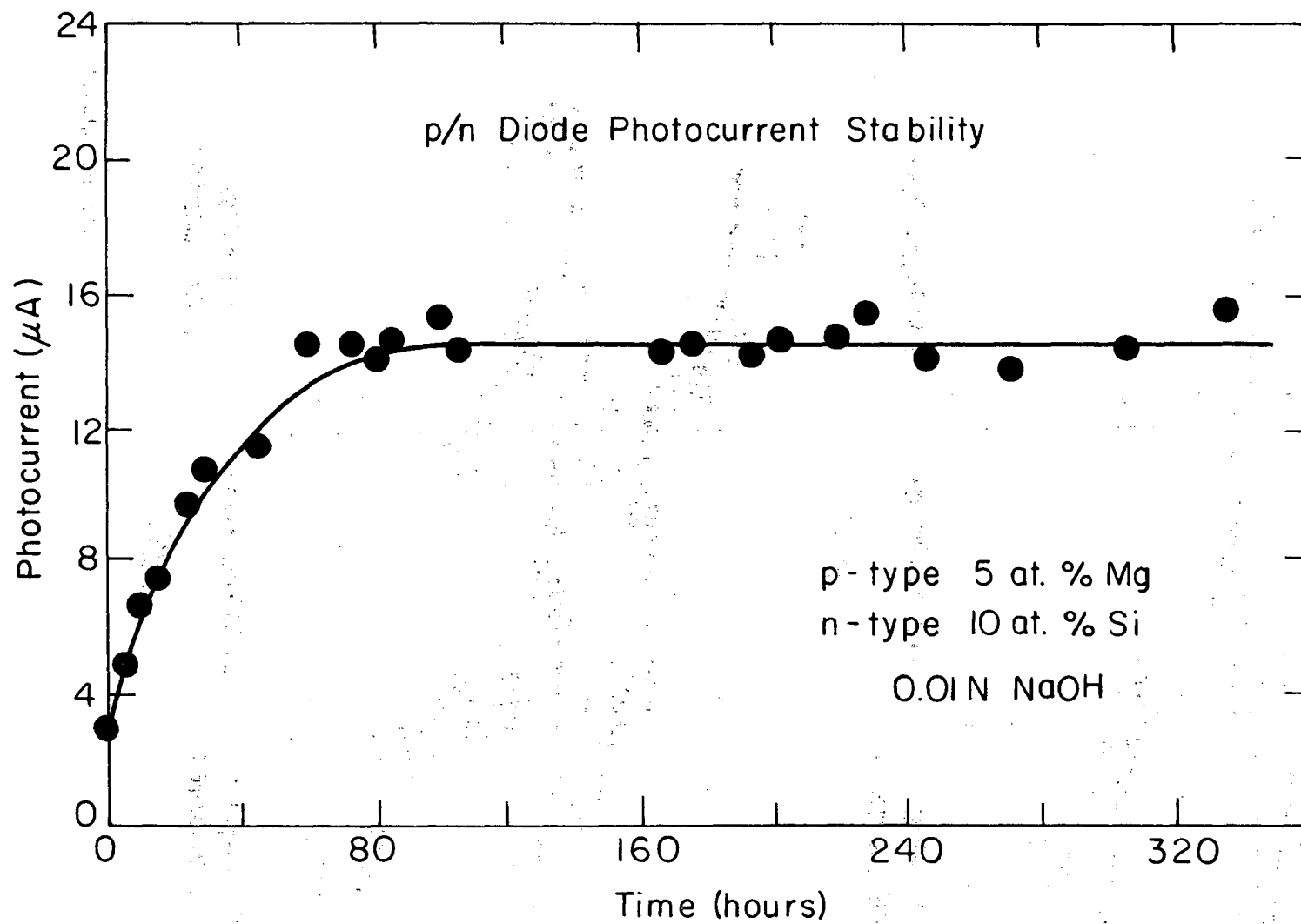
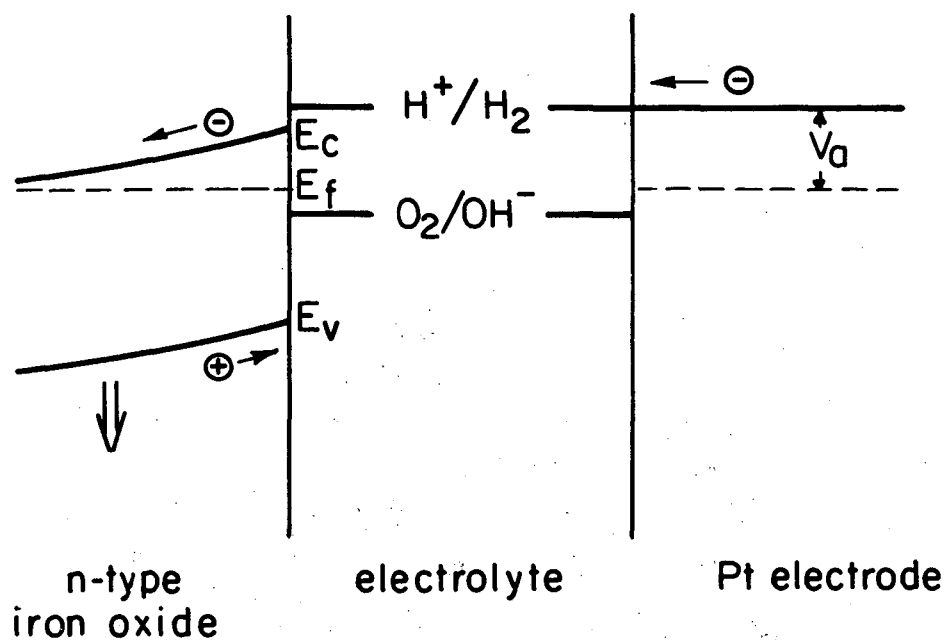
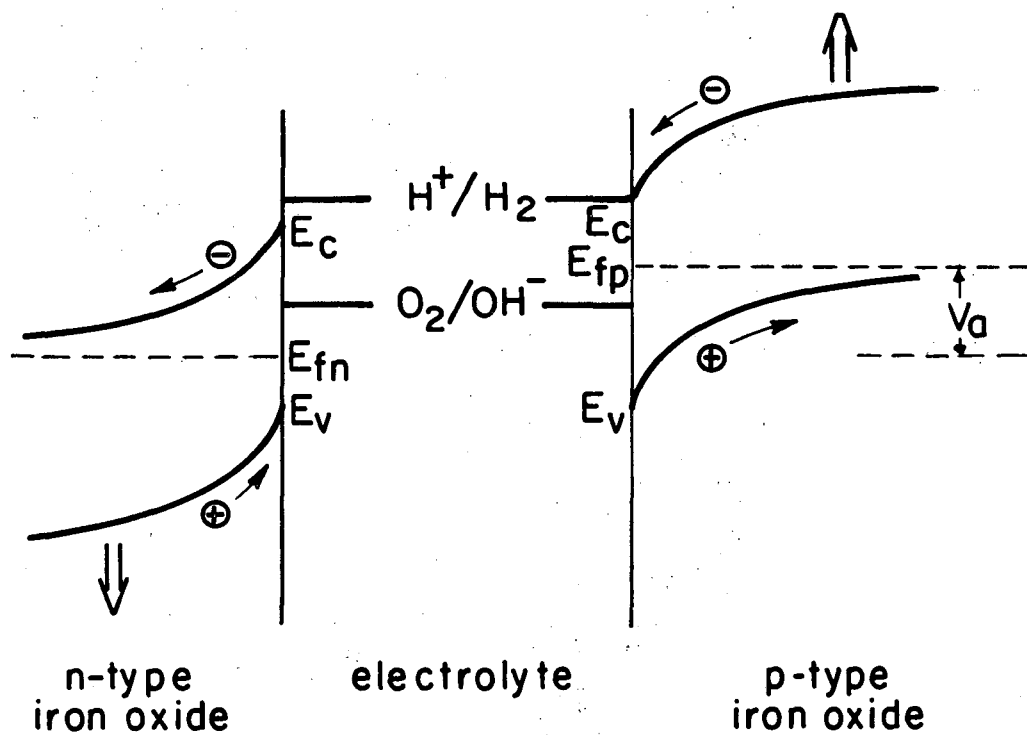


Fig. 5



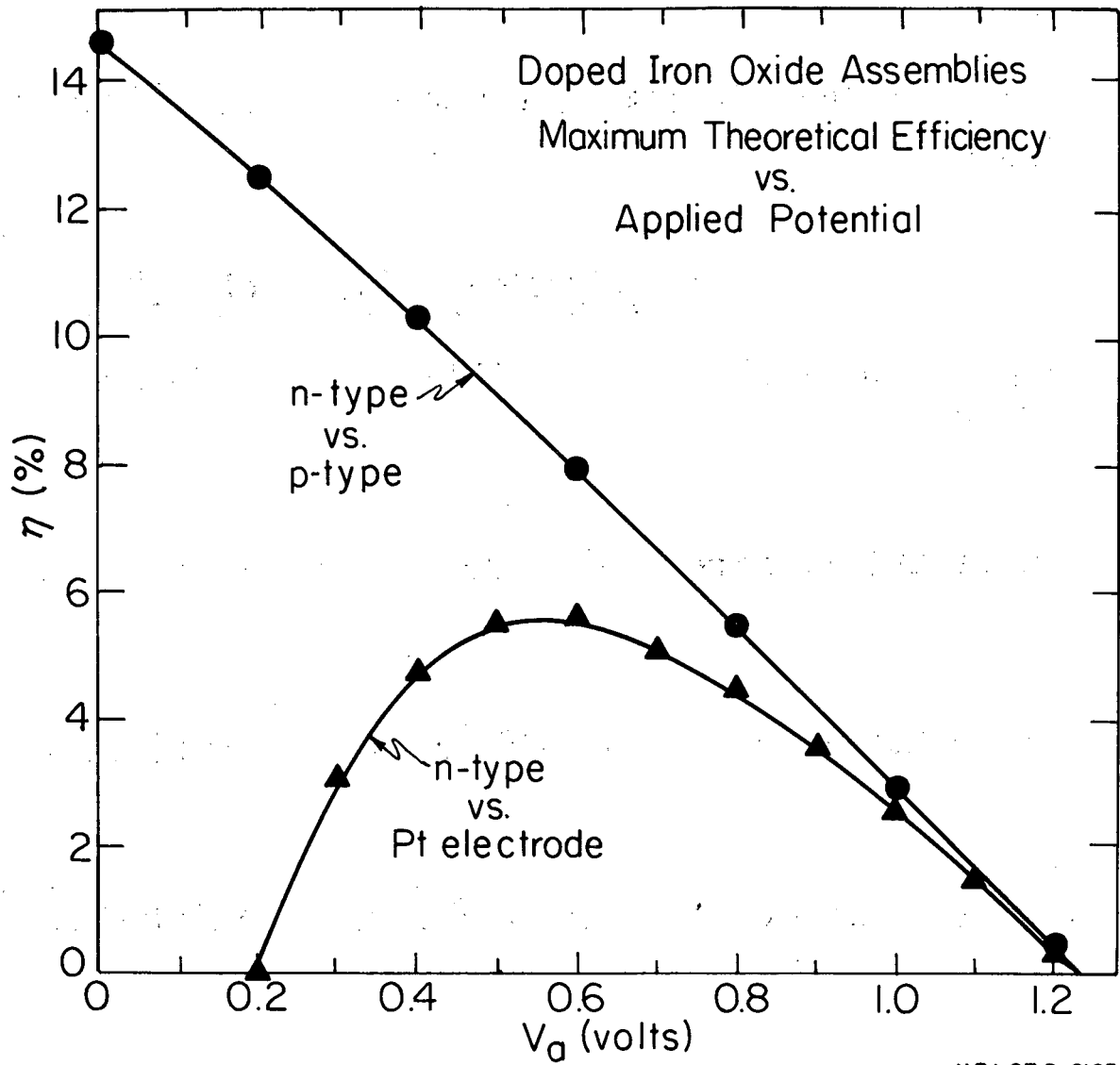
(A)



(B)

XBL 838-6164

Fig. 6



XBL838-6165

Fig. 7

From the Mott-Schottky plots and the energy level diagram we obtain:

	<u>p-type iron oxide</u>	<u>n-type iron oxide</u>
Conduction band edge	~0 mV	~200 mV
Valence band edge	~2300 mV	~2500 mV
Band bending	~1550 mV	~550 mV
Majority carrier concentration	$\sim 5 \times 10^{16} \text{ cm}^{-3}$	$\sim 2 \times 10^{18} \text{ cm}^{-3}$
Depletion layer width	~5000 Å	~500 Å

X BL 836-5786

Table I.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720