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THE UNBIASED P/N ASSEMBLY

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The Photodissociation of Water by Doped Iron Oxides:

The Unbiased p/n Assembly

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ABSTRACT

Mott-Schottky capacitance measurements are used to locate semiconductor band edges for a short circuited p-type/n-type α-Fe₂O₃ assembly in aqueous solution. The thermodynamic feasibility of the catalytic photodissociation of water without external bias is verified for this assembly from an energy level diagram obtained for the electrode/electrolyte interfaces. Photocurrent stability and Auger analysis of the electrode show no evidence of electrode dissolution. Oxygen evolution is monitored from an assembly using mass spectrometry and H₂¹⁸O enriched water.
Recently we reported the production of hydrogen from water by illumination of both electrodes in a Mg-doped (p-type) and Si-doped (n-type) iron oxide assembly. With no applied bias, these polycrystalline electrodes were connected in the short circuited configuration shown in Fig. 1.

Iron oxide is an intrinsic n-type semiconductor with a bandgap of approximately 2.3 eV. Doping with Si enhances this n-type behavior. Nevertheless, when Si-doped iron oxides are employed with a metal cathode in a photoelectrochemical cell to dissociate water, an external bias is generally needed in addition to light of energy greater than this bandgap. Our success in producing hydrogen catalytically with an unbiased cell is due to the implementation of a Mg-doped p-type iron oxide photocathode. The resulting p/n assembly provides a simpler alternative to biased photoelectrochemical systems.

It is the purpose of this communication to present advances in the characterization and stability of this unbiased p/n assembly. We report the determination of the energy level diagram for the short circuited assembly from Mott-Schottky measurements. This establishes the thermodynamic feasibility of hydrogen photoproduction from water without external bias. We also demonstrate improved stability for the device: photocurrents persist undiminished for two weeks with no signs of electrode deterioration. Finally, we show that oxygen is produced catalytically from the cell in addition to hydrogen as reported previously.

In this study, n-type and p-type electrodes were prepared by mixing iron oxide powder (α-Fe₂O₃) with appropriate amounts of SiO₂ or MgO,
respectively. Work reported here used n-type electrodes of iron oxide doped with 10 atomic percent Si and p-type electrodes of iron oxide doped with 5 atomic percent Mg. These mixtures were pressed into pellets, sintered, cooled rapidly in water, then mounted on a conductive backing of silver epoxy. Details of this preparation procedure have been presented elsewhere.\textsuperscript{1,4}

To determine the energy level diagram of the operating p/n iron oxide assembly, band edge locations of both electrodes were determined using a capacitance method suggested by Mott and Schottky.\textsuperscript{5,6} The capacitance of the semiconductor space charge layer ($C_{sc}$) changes with applied potential ($V_a$) according to the relation

\begin{equation}
\frac{1}{C_{sc}} = 2(q\varepsilon\varepsilon_0 A^2 N)^{-1}(V_a - V_{fb}),
\end{equation}

where $\varepsilon$ is the semiconductor dielectric constant, $A$ is the electrode surface area, $N$ is the majority carrier density, and $V_{fb}$ is the position of the Fermi level when there is no band bending.

Capacitances were determined independently for the p-type and n-type iron oxide electrodes in 0.01 N NaOH solution against a Pt counterelectrode. Measurements were made at a frequency of 1.5 kHz under focused illumination from a tungsten-halogen lamp, using a Pine RDE potentiostat, PAR Model 124A lock-in amplifier, and a mercury oxide reference electrode.

In Fig. 2, the inverse square of the space charge capacitance ($\frac{1}{C_{sc}}^2$) is plotted against the applied voltage ($V_a$) for both the n-type and p-type
electrodes. All potentials are reported with respect to a reversible hydrogen electrode (RHE). In this scale the H+/H₂ redox couple lies at 0 mV in electrolyte of any pH. For both electrodes there is a range of potentials where the Mott-Schottky relation is strictly obeyed. By extrapolating to infinite capacitance, the flatband potentials may be extracted as the intercept of these plots. From Fig. 2, flatband values for the n-type and p-type electrodes are 200 mV and 2300 mV (RHE) respectively. Since the slope of the Mott-Schottky plots is given by 

\[ s = \frac{2(q\varepsilon_o A^2N)}{\varepsilon} \] 

one can extract majority carrier concentrations for these semiconductor materials.

Using a measured value of \( A = 6 \text{ cm}^2 \) for the electrodes and the dielectric constant for \( \alpha-\text{Fe}_2\text{O}_3 \) of \( \varepsilon = 100 \), majority carrier concentrations are calculated to be \( N_+ = 5 \times 10^{16} \text{ cm}^{-3} \) for the Mg-doped samples and \( N_- = 2 \times 10^{18} \text{ cm}^{-3} \) for the Si-doped electrodes. Due to a considerable uncertainty in surface area determinations for these polycrystalline samples, charge carrier densities are reliable within an order of magnitude at best.

By using a known value for the \( \text{Fe}_2\text{O}_3 \) bandgap (2.3 eV)² and flatband potentials from the Mott-Schottky measurements, one can construct an energy level diagram for the short circuited doped iron oxide p/n assembly. This is shown in Fig. 3.

For heavily doped n-type semiconductors, the flatband is nearly
coincident with the conduction band edge ($E_C = V_{fb} = 200mV, \text{RHE}$). Conversely, for a heavily doped p-type semiconductor the flatband lies very close to the valence band edge ($E_V = V_{fb} = 2300 \text{ mV, RHE}$). The thermodynamic condition for the photoproduction of hydrogen and oxygen is that the p-type conduction band must be at or above the $H^+/H_2$ half cell potential, while the n-type valence band must lie below the $O_2/OH^-$ half cell potential. These conditions are met by the p/n iron oxide assembly as shown in Fig. 3. Also included in the figure is the location of the Fermi level. Separate measurements against a mercury oxide reference electrode have indicated that the Fermi level of an operating p/n assembly lies at $750 \pm 50 \text{ mV (RHE)}$.

From Fig. 3, the operating details of the short circuited p/n assembly are evident. Upon illumination of both electrodes by bandgap radiation ($h\nu > 2.3 \text{ eV}$), electron-hole pairs are produced in both the n-type and p-type electrodes. In the n-type material, holes driven toward the electrode/electrolyte interface mediate the conversion of $OH^-$ ions in solution to $O_2$ gas. Electrons driven toward the surface of the p-type electrode reduce $H^+$ ions to $H_2$ gas. At both electrodes, majority carriers diffuse away from the surface to contribute to the observed photocurrents.

Both redox couples in solution ($H^+/H_2$ and $O_2/OH^-$) lie at energies such that the simultaneous evolution of $H_2$ and $O_2$ is thermodynamically feasible. While there is a favorable potential drop of about 1.27 volts for oxygen production at the n-type electrode, electrons in the p-type photocathode reach the electrolyte
with energies very near the potential of the $\text{H}^+/\text{H}_2$ redox couple.

Butler and Ginley\textsuperscript{8} have proposed a model in which a dopant atom with a lower electron affinity than atoms in the host lattice shifts semiconductor band edges toward more cathodic potentials. This effect was observed in our p-type Mg-doped iron oxide. The addition of 5 atomic percent Mg (EA = 1.2) to Fe (EA = 1.7) shifts band edges in the p-type electrode several hundred millivolts towards more cathodic potentials as compared to undoped Fe$_2$O$_3$\textsuperscript{9}. This shift is sufficient to line up the conduction band and $\text{H}^+/\text{H}_2$ redox couple so that hydrogen production becomes energetically possible.

Fig. 3 shows that the band bending near the surface of the n-type iron oxide is about 550 mV, while at the p-type iron oxide surface this bending is greater than 1500 mV. Correspondingly high field gradients in the space charge layer minimize electron-hole recombination, making it possible to sustain the quantum efficiencies of $\eta = 5 \times 10^{-4}$ we have found in these polycrystalline assemblies.

We reported earlier that the hydrogen production and photocurrents produced by an iron oxide p/n assembly gradually declined. After about 8 hours of illumination the photoactivity of an assembly would diminish to zero. Surface analysis using Auger electron spectroscopy has shown that this decline was most likely due to poisoning of the electrode surfaces by organic contaminants dissolved in the electrolyte solution. To eliminate the contamination, more recent experiments were performed in an all glass cell with conductive leads isolated from the electrolyte.
solution by silicone rubber sealant. In addition, doubly distilled water (specific resistance greater than \(2 \times 10^6\) ohm cm\(^{-1}\)) and reagent grade NaOH were used to prepare the electrolyte (0.01 N NaOH).

As seen in Fig. 4, an assembly tested in this configuration shows excellent long term stability. At first exposure to solution, the photoactivity was quite low \((I_{ph}=3\mu A)\). However photocurrents were found to steadily increase over an 80 hour period to a stable value of \(I_{ph}=15\mu A\). Once steady state behavior was established, photocurrents persisted undiminished throughout 320 hours of continuous illumination. With a surface roughness factor of 10 for these electrodes (as established by BET surface area measurements), \(H_2\) production totalled more than 5000 monolayers, clearly proving the catalytic nature of the hydrogen photoproduction process.

At this point, reasons for the activation period are not understood. ESCA studies are underway to investigate both the slow formation of hydroxylated intermediates or oxidation of near surface layers as possible causes.

A comparison of Auger scans before and after extended operation showed virtually no change in surface composition of either electrode. These results are consistent with the findings of other investigators\(^10\), who have found iron oxide to be extremely stable in aqueous solution over a wide range of pH.

While an unbiased p/n assembly was found to produce hydrogen from water at a rate which correlated well with observed photocurrents, the detection of oxygen was not previously attempted. Therefore we carried out experiments to monitor
oxygen production from the assembly as well. Measurements were performed in 0.01 N NaOH, using water isotopically labelled with 6% H\textsuperscript{18}O (Alpha-Ventron \textsuperscript{2} Distributors). Gas samples were collected over an assembly illuminated in this solution. Mass spectrometry verified the production of \textsuperscript{34}O\textsubscript{2}: direct evidence that water molecules were dissociating to form oxygen gas.

Fig. 5 shows the \textsuperscript{34}O\textsubscript{2} partial pressure as a function of time. When the p-type and n-type electrodes were isolated (open circuit configuration), there was no photocurrent and the \textsuperscript{34}O\textsubscript{2} partial pressure remained constant. However when the circuit was closed, the concentration of \textsuperscript{34}O\textsubscript{2} increased. In addition to establishing that oxygen is produced in a photoactive process, these results indicate that oxygen is evolved directly from the water and not from dissolution of the iron oxide electrode.

Oxygen has a high solubility in water (1.91 cm\textsuperscript{3} per 100 cc)\textsuperscript{11}. Therefore much of the oxygen produced in our tests remained dissolved in solution. However calculations comparing observed rates of \textsuperscript{32}O\textsubscript{2} and \textsuperscript{34}O\textsubscript{2} production and considering this oxygen solubility show fairly good correspondence (within 20%) between total oxygen yield and integrated photocurrents.

From this work, it appears that p/n iron oxide assemblies employed without the use of external potential are a viable alternative to biased n-type or p-type semiconductor devices for solar energy conversion. While quantum efficiencies are low, the device as fabricated is far from optimal. The electrodes are polycrystalline, heterogeneous in composition, and the doping levels are uncontrolled.
With careful investigation and modification of these and other factors currently limiting quantum efficiency, hydrogen may eventually be produced economically in a simple, passive photoelectrochemical cell.

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FIGURE CAPTIONS

Fig. 1: Schematic of the unbiased p/n assembly. Photodissociation of water into hydrogen and oxygen occurs when both electrodes are illuminated by light of energy greater than the iron oxide bandgap.

Fig. 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 \(f = 1.5\) kHz in 0.01 N NaOH against a Pt counterelectrode.

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

Fig. 4: Photocurrent stability for the unbiased p/n assembly. Illumination at both electrodes was approximately 35mW/cm\(^2\), provided by 500W tungsten halogen lamps. Following an 80 hour activation period, photocurrents remained stable throughout 320 hours of continuous illumination.

Fig. 5: Oxygen production from the p/n assembly. Mass spectrometry was used to monitor \(^{34}\text{O}_2\) production from water enriched with isotopically labelled \(^2\text{H}_2\text{O}\).
REFERENCES


Fig. 1

An Ammeter is connected to a system involving a photoanode and a photocathode. The photoanode is n-type Si-doped Fe₂O₃, while the photocathode is p-type Mg-doped Fe₂O₃. The system is immersed in 0.01 N NaOH. Hydrogen (H₂) and oxygen (O₂) are produced as a result of the photoelectrochemical reaction. The system is illuminated by light (hv).
n-type electrode
Si/Si + Fe = 10 atom %

\[ V_{fb} = +0.2 \text{ V (RHE)} \]
\[ N_D = 2 \times 10^{18} \text{ cm}^{-3} \]

p-type electrode
Mg/Mg + Fe = 5 atom %

\[ V_{fb} = +2.3 \text{ V (RHE)} \]
\[ N_D = 5 \times 10^{16} \text{ cm}^{-3} \]
ENERGETICS OF CONNECTED P-TYPE AND N-TYPE IRON OXIDES

Fig. 3

P-TYPE SEMICONDUCTOR

ELECTROLYTE

N-TYPE SEMICONDUCTOR

ELECTROCHEMICAL SCALE (VOLTS, RHE)

XBL 832-518IA
Fig. 4

p/n Diode Photocurrent Stability

Photocurrent (μA)

Time (hours)

p-type 5 at. % Mg
n-type 10 at. % Si
0.01 N NaOH

XBL 833-8744
Fig. 5
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