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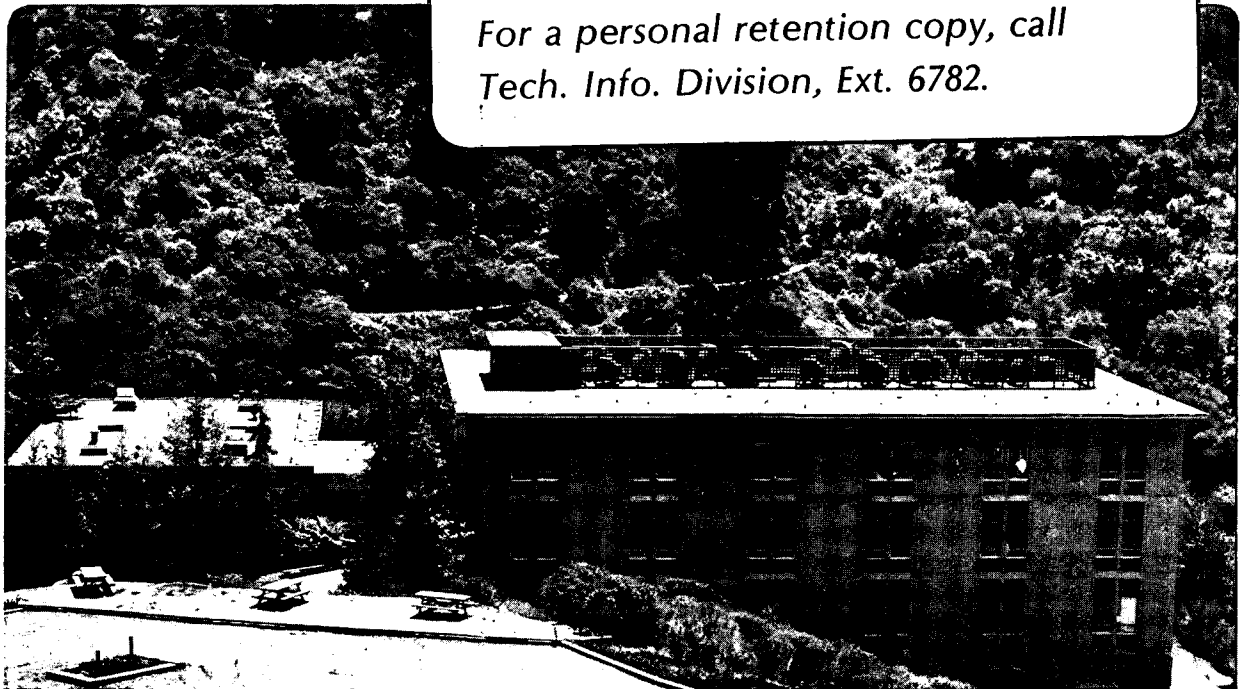
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April 1984

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CATALYZED PHOTODISSOCIATION OF WATER - THE FIRST STEP IN INORGANIC PHOTOSYNTHESIS

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INTRODUCTION

Since 1972 there has been intensive research into the photodissociation of water using a variety of surfaces as catalysts. From its origins in electrochemistry¹ this area of investigation has become an important subfield of both surface science and heterogeneous catalysis.² Much of the theoretical basis for semiconductor photoelectrolysis has been developed by Gerischer.³

Dissociation of water can occur at a semiconductor surface when an incident photon of suitable energy generates an electron and an electron vacancy in the conduction and valence bands of the solid, respectively (Figure 1). The electron may then reduce a hydrogen ion at the surface to a hydrogen atom ($H^+ + e^- \rightarrow H$), which combines with another to form H_2 gas. Conversely, the electron vacancy can capture the negative charge from a hydroxyl ion at the surface ($OH^- + h^+ \rightarrow OH$). Subsequent dimerization of the unstable radical will yield a peroxide molecule H_2O_2 which decomposes and releases oxygen.

When both oxidation and reduction occur at the same surface (type I system) as in the case of strontium titanate, the photochemical reaction is similar to the silver halide photographic process. However, photodecomposition of the solid does not take place. Instead, water adsorbed at the surface is dissociated. In another configuration, hydrogen ions are reduced at one surface and hydroxyl ions are oxidized at another surface (type II system). In this arrangement, light irradiates both surfaces which are electrically connected to permit the free flow of charges between sites at which the reduction and oxidation processes occur. The two electrode p-type (Mg-doped) and n-type (Si-doped) iron oxide

photochemical diode is an example of this type of system. Figure 1 shows both of these configurations which can be used for the photodissociation of water.

The substantial adsorption of light of band gap or higher energy by the semiconductor makes solar energy conversion via this intermediate electronic process much more efficient than a direct electronic excitation and dissociation of the molecules by incident light.

There are specific thermodynamic criteria which must be satisfied for this process to be feasible. The conduction band edge of the semiconductor in solution must lie at a potential more positive than the $H^+ + e^- \rightarrow H$ half cell potential. Similarly, the valence band edge of the semiconductor must be more negative than the $2OH^- \rightarrow 2e^- + O + H_2O$ half cell potential. These requirements dictate that the semiconductor band gap be greater than 1.23 eV, the one electron potential needed to dissociate water ($H_2O \rightarrow H_2 + 1/2 O_2$, $\Delta E^\circ = 1.23$ eV).

There are a number of semiconductors which satisfy these basic thermodynamic criteria. However, a large proportion of these undergo side reactions in aqueous solution which result in corrosion or decomposition of the surface, rendering them inactive. From the standpoint of stability, many of the transition metal oxides are excellent candidates. Figure 2 shows the valence and conduction edges for a number of oxides.

Over the past seven years we have carried out surface science studies of the complex mechanisms that lead to the photochemical decomposition of water over two transition metal oxides: strontium titanate (type I) and iron oxide (type II). We have utilized electron spectroscopy techniques (photoelectron, auger electron, and electron loss) to monitor the surface

composition and oxidation states of surface atoms. Other techniques use a reaction cell which permits monitoring of photocurrents as well as the evolution of gases (H_2 and O_2) generated by the photoreaction. As a result, many of the elementary reaction steps leading to H_2 and O_2 evolution have been identified. In this paper we review what has been learned and suggest directions of research so that hydrogen produced from water and solar radiation may become a feasible source of energy.

$SrTiO_3$ is an n-type semiconductor with a band gap of 3.1 eV. As a consequence, light in the near ultraviolet energy range is needed to excite electrons from the valence into the conduction band. The highest rate of hydrogen generation (0.05 hydrogen atoms per absorbed photon) was found when $SrTiO_3$ crystallites partly reduced in a hydrogen furnace at elevated temperature, covered with islands of platinum, and then immersed in an alkali hydroxide solution of considerable ionic strength.

Each of these treatments addresses a particular step in the water photodissociation process. Reduction of $SrTiO_3$ at high temperatures renders the surface rich in Ti^{3+} ions as determined by a combination of surface science techniques.³ While the reaction occurs without platinum, there is a fifty-fold increase in the water dissociation rate⁴ in the presence of the metal. Platinum catalyzed the recombination of hydrogen atoms to molecules, an important reaction step which occurs only slowly on the oxide surface. Alkali hydroxides are needed⁵ to catalyze the hydroxylation of the oxide surface. The photodissociation of H_2O to H^+ and OH^- at the surface is one of the important steps toward the formation of H_2 and O_2 and the hydroxylated oxide surface is an essential intermediate in this process.

Surface studies have shown⁶ that the Ti^{3+} ion is oxidized upon water adsorption and rereduced with the help of the photoelectron. It is also known from isotope labelling experiments that the lattice oxygen at the surface readily exchanges with oxygen in the adsorbed water molecules. From these surface science and reaction rate investigations the catalytic reaction cycle shown in Figure 3 has been proposed to describe the photodissociation of water over $SrTiO_3$ surfaces. Oxidation and reduction between Ti^{3+} and Ti^{4+} and the reversible hydroxylation of the oxide surface can be seen to be interrelated and essential reaction steps in the dissociation of water.

By understanding and facilitating the elementary steps in this process, we have optimized water dissociation by ultraviolet light with the $SrTiO_3/Pt/NaOH$ system. Using microscopic information obtained on the mechanism of water dissociation over $SrTiO_3$, we can search for similar materials which use a wider range of the solar spectrum to split water to H_2 and O_2 . This search led us to the development of the iron oxide semiconductor system.

Iron oxide has a complex phase diagram that is shown in Figure 4, consisting of at least three distinct iron-oxygen compounds. Fe_2O_3 is an intrinsic n-type semiconductor with a band gap of 2.3 eV. The divalent oxide, FeO , is a p-type semiconductor with a band gap also near 2.3 eV. The mixed oxide, Fe_3O_4 , is a low resistivity compound, almost metallic. In preparing separate sites for the oxidation and reduction processes, it was necessary to enhance the n-type or p-type iron oxide behavior respectively.

The n-type phase, Fe_2O_3 , has a valence band appropriately located (see Figure 2) for oxygen evolution from the reduction of OH^- species.

Doping Fe_2O_3 with Si enhances this n-type behavior by improving the photoconductivity of iron oxide. As shown in Figure 5, we find anodic photocurrents corresponding to oxygen production if we apply a potential to the electrode greater than +400 mV with respect to the hydrogen evolution potential (RHE).

For the photocathode, one needs a p-type material to reduce hydronium ions (H_3O^+) in the solution to hydrogen gas. We have found that by quenching a mixed oxide of Fe_2O_3 and MgO, we can stabilize a near surface FeO phase, which has the p-type character we need. Figure 5 shows that for an applied potential less than 900 mV, RHE photocurrents appear corresponding to hydrogen evolution from this p-type electrode. The p-type region of the Mg-doped sample was restricted to the first few microns at the surface reflecting the conditions of formation of the FeO-phase at the surface upon rapid quenching from high temperatures ($\sim 1400^\circ\text{C}$). We have also found that the p-type FeO phase may be obtained in a thin film form without Mg doping by the use of plasma sputtering in vacuum.⁷

The individual electrodes require an external potential for gas production. When connected together, however, the p/n assembly assumes an intermediate potential so that gas is evolved from both electrodes. When the n-type (Si-doped) and p-type (Mg-doped) samples were illuminated in basic solution, a photocurrent of $15\mu\text{A}$ was observed, and H_2 and O_2 evolution occurred without the use of an external potential. Photoelectrochemical determination of band edges for the individual electrodes⁸ permitted the construction of a potential energy diagram of the p/n iron oxide assembly as shown in Figure 6. From this representation of the semiconductor/solution interfaces, the operation of the iron oxide p/n assembly is readily understood.

Photocatalyzed dissociation of water represents the first important step in photosynthesis, the production of oxygen and a reactive intermediate, hydrogen. The subsequent reactions of H_2 with CO_2 to produce hydrocarbons or organic molecules containing oxygen are exothermic. These reactions will occur readily without illumination on suitably catalysts in the appropriate temperature range. Iron oxides themselves are known to be excellent catalysts for the reactions of CO or CO_2 with hydrogen (CO_2 is readily converted to CO via the so-called water gas shift reaction, $CO_2 + H_2 \rightarrow CO + H_2O$). It appears then that "inorganic photosynthesis" using iron oxide surfaces may be possible by utilizing photocatalyzed water dissociation followed by the catalytic reactions of hydrogen with CO_2 . In fact, these processes may have been important in synthesizing small organic molecules in the prechlorophyll era of our planet. It should be noted that magnesium and iron containing silicates are the most abundant minerals in the earth's mantle.

Practical applications of this method of solar energy conversion will require an increase in the efficiency of the process (currently about 0.1%) by over an order of magnitude. It appears that a surface reaction step may control the efficiency rather than bulk properties of the materials. Imaginative research to identify the important reaction steps and acceleration of these rates by the use of added catalysts could convert this interesting field of surface science into a new chemical technology.

ACKNOWLEDGEMENT

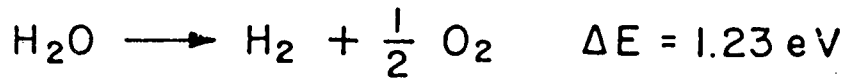
This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

FIGURE CAPTIONS

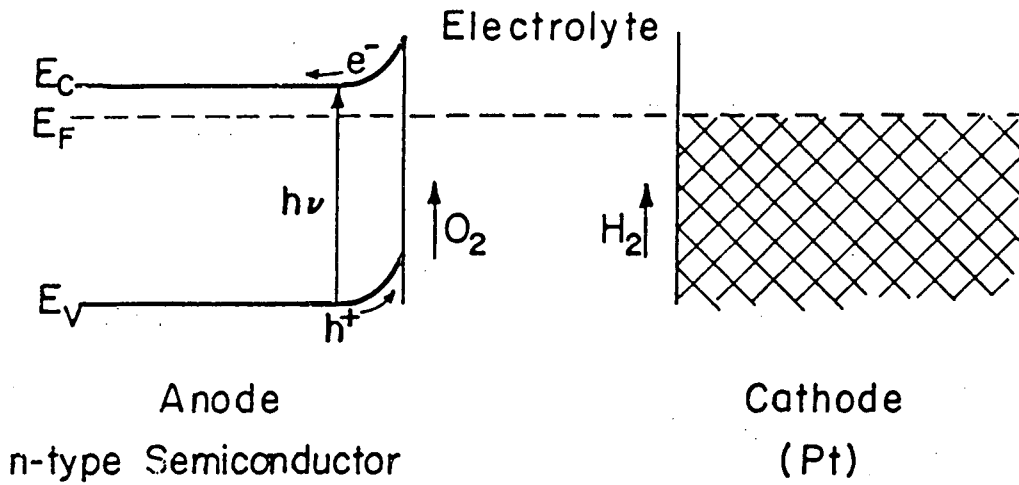
- Figure 1: Energy level diagrams for semiconductor/metal and semiconductor/semiconductor photoelectrolysis cells.
- Figure 2: Valence and conduction band edges for several transition metal oxides. Also included are potentials for hydrogen and oxygen evolution.
- Figure 3: Mechanism for photodissociation of water over SrTiO_3 .
- Figure 4: Iron-oxygen phase diagram.
- Figure 5: Photocurrent vs. applied voltage for n-type and p-type electrodes against a Pt counterelectrode. Anodic photocurrents correspond to oxygen evolution, cathodic photocurrents to hydrogen evolution.
- Figure 6: Energy level diagram for an operating p-type/n-type iron oxide assembly.

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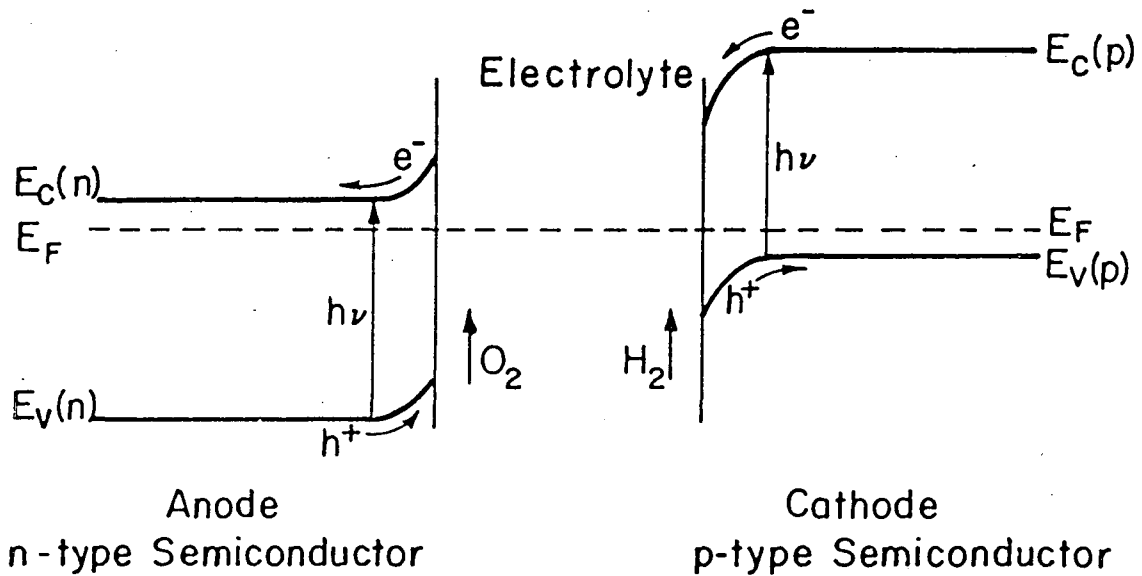
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Semiconductor - Conductor Cell

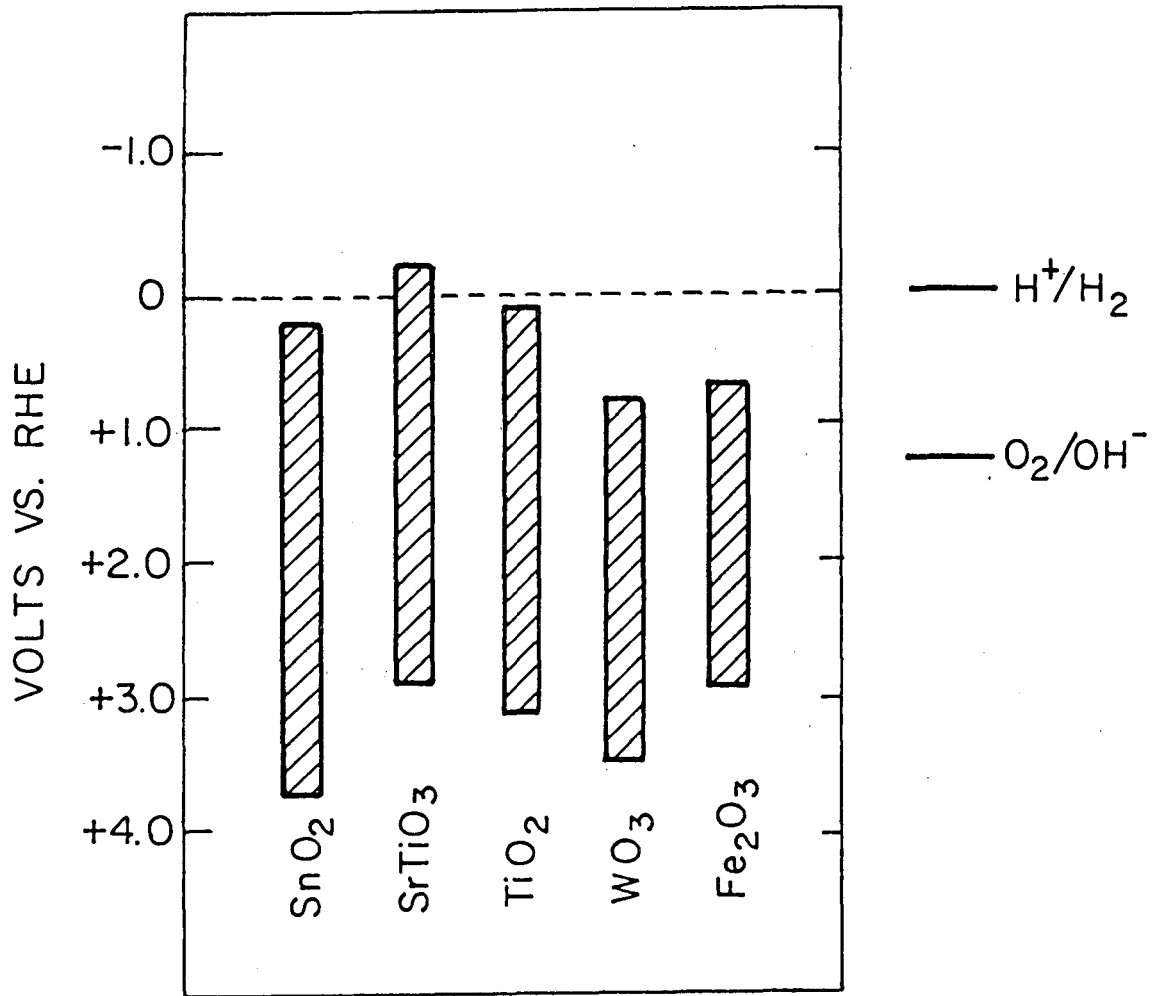


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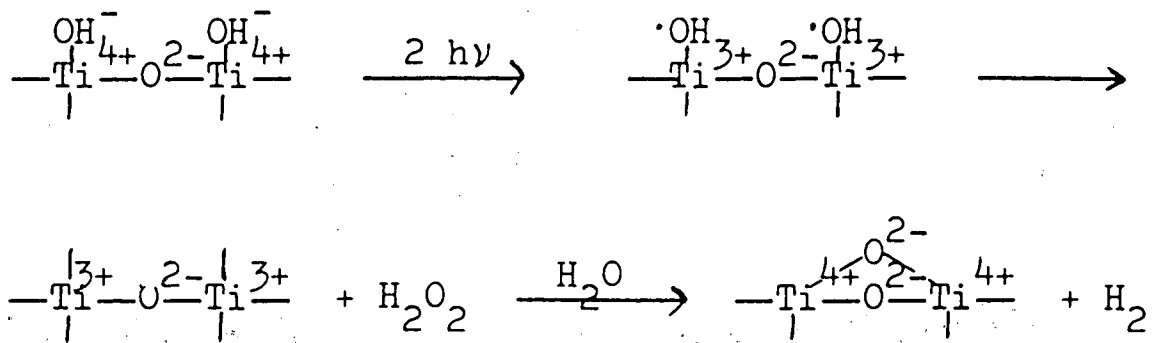
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Fig.1



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Fig. 2



Van Damme and Hall, JACS 101 4373

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Fig.3

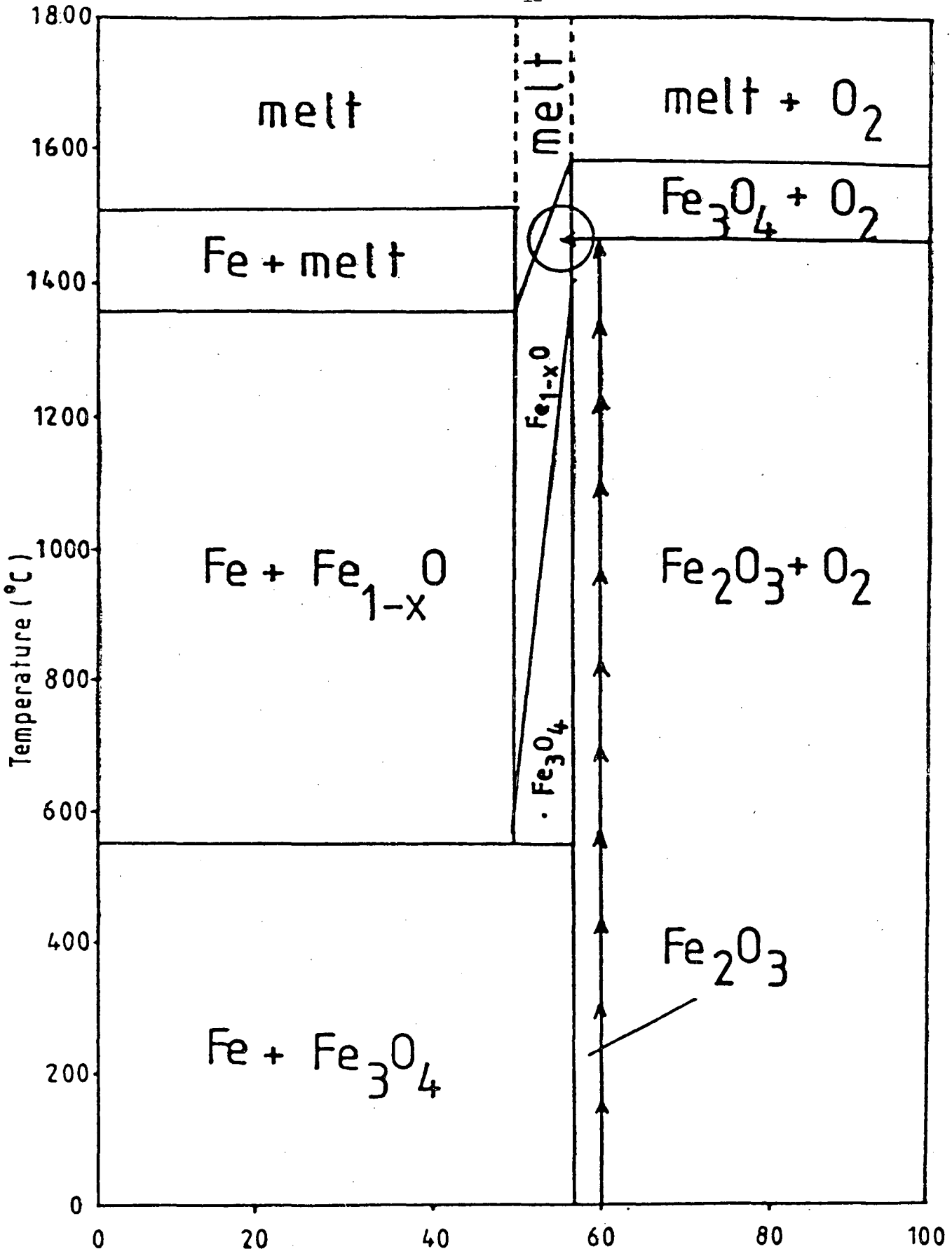
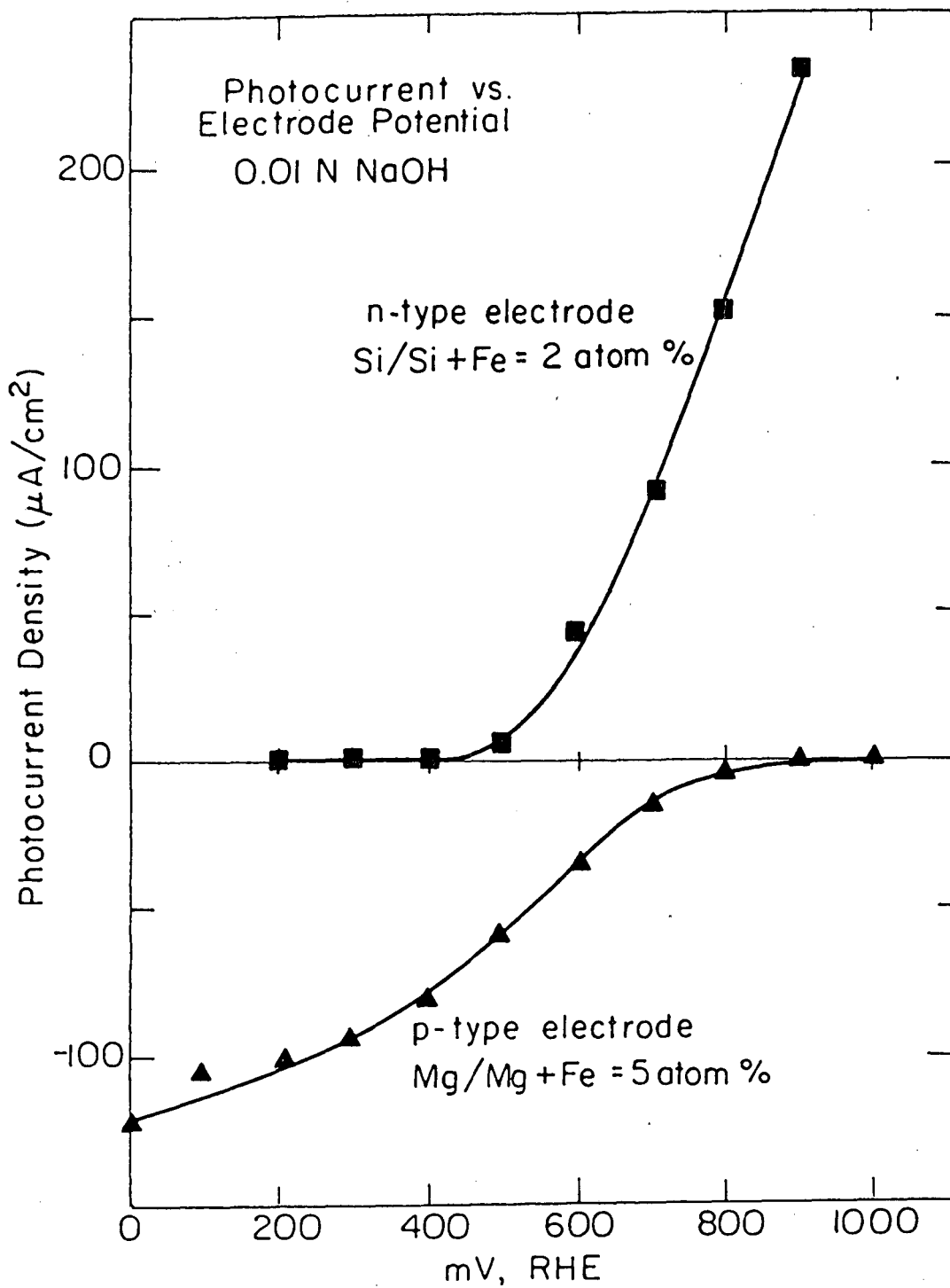


Fig.4

Atomic Percent Oxygen

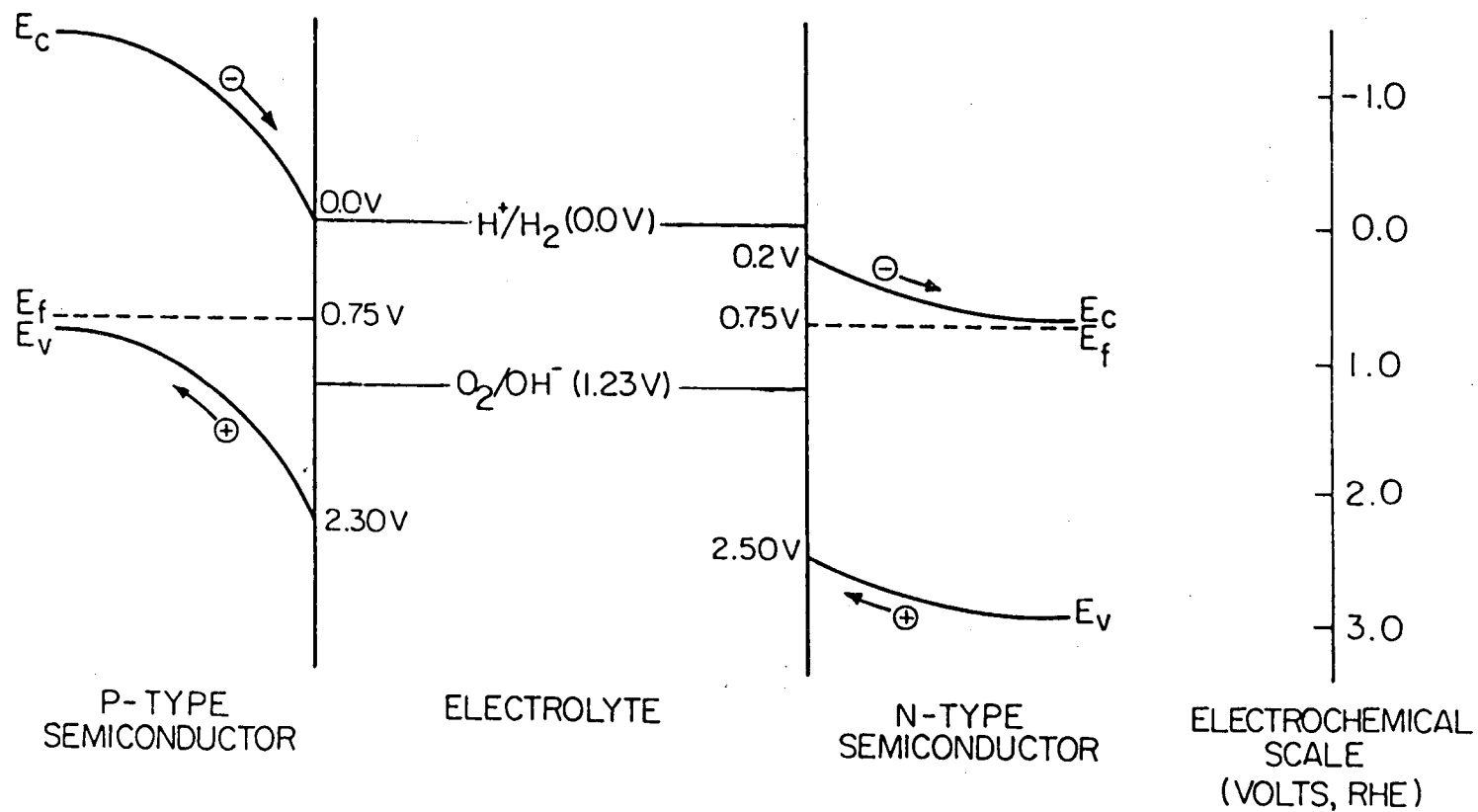


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Fig.5

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

Fig. 6



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