

CHAPTER VI

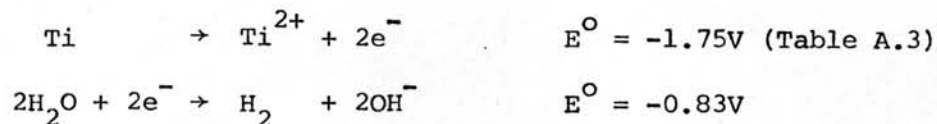
DISCUSSION

An important problem encountered in this study was the measurement of exact intensities of sunlight with time so that exact photocell efficiencies can be computed. In this study the intensities for a particular run were averaged over used. This approach some advantages and inconveniences in the present context. The major disadvantage was the unsuitability of comparing the data with other data in which accurate sunlight intensities measurement equipment was used. However, the average intensities were useful in this study to report results of photocells under different test conditions. Therefore the solar conversion efficiencies of η_1 , η_2 and η_4 used in this experiment are average values.

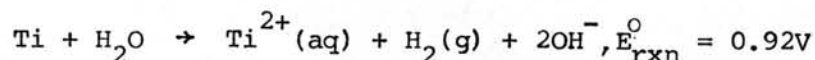
6.1 Effect of Thickness of TiO_2 Film

Photocurrents under sunlight for each groups in Table 5.2.3a are equal . By comparing conversion efficiencies (η_2) of each groups under the same conditions it is shown that electrode D is better than the others in Table 5.2.3c. Under spot light, the photocurrents are not different for each electrode and are much lower than under sunlight illumination because TiO_2 electrodes absorb short wavelenghts light, the spot light could not give this range of light to the electrodes. The suitable lamps for this spectrum are xenon or mercury lamps. Therefore, in simple tests of the measurement of the photocurrent one must operate the photocells under the 300-400 nm spectrum using such lamps and the photoresponse comparison for each electrodes should also involve the study of their I-V characteristics.

In this experiment, the short circuit photocurrent of each electrodes are not enough to test effects of the TiO_2 thickness. Note that the dark currents (I_d) of electrodes must be measured because titanium metal can react with water molecules, as follow:



the overall reaction



This reaction easily occurs at room temperature ($\Delta G < 0$). If some parts of the Ti-pieces are not completely oxidized to form a TiO_2 film and the coating of epoxy resin is not done carefully, the above reaction occurs and the cell will be a galvanic cell (see Appendix A.3), gives an emf of about 0.92 V. This measurement of I_d is useful to check this effect.

The rates of hydrogen evolution in Table 5.2.4b show stability of each electrodes in group A, B and C for about 1 hr. For the B electrodes TiO_2 surfaces showed some cracks after for more than 40 minutes run. Their preparations were not so good as electrodes of C group (in Table 5.2.1a) because of the large area (2X3 cm) and the long heating time.

For the average intensities of about 65 mW/cm^2 , the hydrogen production rates of photocells with D electrode (3-4 μm) are more than the A electrode (1 μm) by about a half, as shown in Figure 5.2.4b. During the day, the rate of hydrogen evolution increases when intensities increases. The results are shown with electrodes of group A, D+C and mixed in Figure 5.2.4c. At low intensities, the rates of each groups are slightly different, and

very different for high intensities. The D+C electrodes are the best with rates higher than the others.

The absorption of photon is depend on the thickness of TiO_2 layer. The absorption curve is characterized by an exponential with defined by absorption coefficient (in Eq. 3.8). Therefore, photo-generated carriers increase with the thickness of TiO_2 and will be maximized at an appropriate thickness. However, TiO_2 thickness of electrodes in this experiment was the range of 1-4 μm , may be not near the maximum point. Thus D+C electrodes ($\sim 4\mu\text{m}$) are better than A electrodes ($\sim 1\mu\text{m}$) for hydrogen production in photocells.

6.2 Effects of Temperature of Solutions

From Figure 5.2.5, the rates of hydrogen evolution are slightly different, at high intensities, the rates of low temperature solution are greater than those at room temperature but at low intensities the rates at room temperature are slightly different from the others. In 4.1.4, the semiconductor will lose its extrinsic nature and becomes intrinsic when the temperature increases, then excess carrier concentration will be negligible and the efficiency will be large at low temperature, but in this experiment, this effect on the efficiencies or hydrogen rates are small because TiO_2 films were not doped with any donor atoms.

At low intensities, the rates at low temperature are less than those at room temperatures. The above effect may be unimportant, but the heat absorbed by the solution of water electrolysis will be a major effect (see 4.1.1), in Figure 4.1.1, raising the temperature lower the voltage at which water can be decomposed.

Effects of temperature in this experiment do not indicate clearly and show exact results of photocells at low and room temperatures, but it may be an interesting effect to study in the future.

6.3 Increasing the Rates of Hydrogen Evolution

During the formation of hydrogen molecules in photocells, an electron-hole pair is generated by photons of sunlight activating TiO_2 atoms at the anode electrode. The electrons will flow through an external circuit to the Pt electrode and react with hydrogen ions in the solution to form hydrogen molecules at the surface of Pt electrode (Figure 6.3b). The presence of those molecules will form a bubble which will flow up to displace the water in the burette. During bubble formation the area of Pt electrode contacting the solution will be reduced, and slow hydrogen formation. A stirred solution will accelerate some bubbles at the Pt surface to detach from the Pt surface.

The results, from Figure 5.2.6 the hydrogen rates increase slightly in a stirred solution. In this system, the Pt electrode is in the burette (Figure 6.3a), thus the stirred solution slightly accelerates the bubbles.

For the photocells used in this experiment, the pH-bias drives the TiO_2 electrodes used for hydrogen evolution under sunlight. Therefore some voltage-bias will increase the hydrogen rates, as in this photocells are biased by solar cells (0.5V, 200 mA), the rate increases are twice the rate of non-biased photocells in Figure 5.2.7a. From Figures 5.2.3a and b show the maximum voltage for photocells with maximum efficiencies, and they are about 0.4 and 0.6 volts at 46 mW/cm^2 and 71 mW/cm^2 of the sunlight, respectively, thus one solar cell may be used to bias the photocells with 0.5 volts. However, the efficiencies of biased photocells (η_4) are equally the non-biased photocells (η_1) in Table 5.2.7 and Fig. 5.2.7b. Increasing the hydrogen rates by a solar cell voltage-bias should be investigated further.

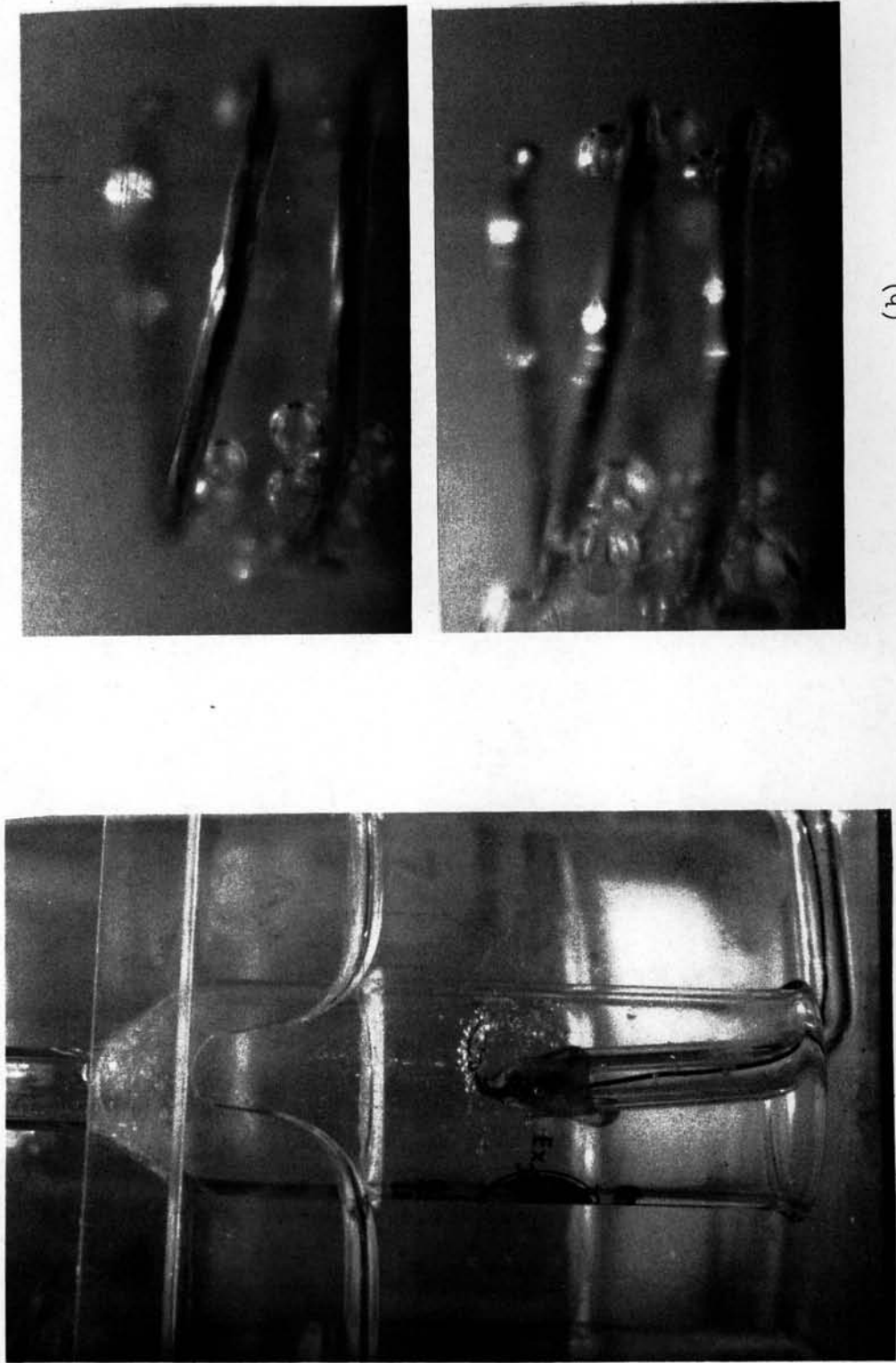


Figure 6.3 Photographs of hydrogen evolution at the platinum electrode

To increase platinum area in photocells, 0.28 cm^2 , 0.45 cm^2 and 0.99 cm^2 areas were used in order to increase the hydrogen rates. Figure 5.2.8a shows the increasing rates due to increased platinum area, with TiO_2 area fixed at about 33.9 cm^2 . But for a small TiO_2 area of 11.6 cm^2 the small area of 0.45 and 0.28 cm^2 for platinum are better than the large area of 0.99 cm^2 in Figure 5.2.8b. From the methods of improving the efficiency of a water electrolysis cell, the surface of electrode should be maximized to reduce the overpotential, see in 4.1.1. Therefore the proper TiO_2/Pt area ratio will yield an efficient system for a photocell for hydrogen production.

To increase the hydrogen rates by stirring the solution, the voltage-bias from a solar cell and the proper of TiO_2 and Pt area, the studies of these effect in photocells should be investigated under constant illumination with light sources (xenon or mercury lamp) in order that the experimental results be more accurate. In the present experiment all effects are studied from photocells under sunlight with variable intensities. Therefore, the results only roughly indicate the various effects in photocells.

6.4 Gold as the Cathode Electrode

Gold was used for the cathode electrode in order to study the hydrogen rates of photocells with system (TiO_2 -Au electrodes). This system was used to study the reduction of cost of electrode because platinum electrodes are expensive. However, the hydrogen rates in photocells with Au electrode are much lower than Pt electrode, as shown in Figure 5.2.9. Table 3.4.1 shows the platinum with a small exchange current and Pt electrode is better than Au as electrode for the hydrogen-evolution reaction as discussed in 3.4.1 (p.25-26).