Progress in Photovoltaic Technology: The Advent of Dye Sensitized Semiconductors

Jonathan T. Goodman Literature Seminar November 9, 1995

The production of electrical energy is one of the largest industries in the United States (2.8×10^{12} kWh in 1991). Power production is limited by the availability of natural resources, environmental concerns, and poor energy conversion efficiencies [1]. The only truly inexhaustible source of energy is solar radiation. The flux of solar energy incident with the atmosphere amounts to approximately 1.7×10^{17} W per year, 2.7×10^{4} times human consumption [2]. The possibility of the direct conversion of light to electrical energy was first recognized in the photoelectrochemical cell reported by Edmond Becquerel in 1839. The study of modern photovoltaic systems began in 1954 with the work of Chapin, Pearson, and Rappaport [3]. These solid state photovoltaic cells are based on 1) p- or n-type doping to redistribute the charge density across the band gap and 2) semiconductors with narrow band gaps, i.e. GaAs (1.4 eV), CdSe (1.7 eV), c-Si (1.1 eV), [4] which absorb the majority of incident light.

The cell efficiency is dependent upon the ability of the cell to absorb incident light and preserve charge separation. The wavelength of light absorbed is directly dependent upon the width of the band gap [4]. The maximum theoretical efficiency for a single band gap material is dependent upon the absorption overlapping with solar radiation, i.e. for E_g=1.5 eV and an air-mass ratio of 0, the maximum efficiency is only 40.7% [5,6]. The doping of a semiconductor changes the potential energy of the Fermi level. Dopants change the concentration of holes in the valence band and electrons in the conduction bands by localizing charge on the dopant. When a hole-doped material is brought in contact with an electron-doped material, a p-n junction is formed and a potential develops across the interface of the two materials. A similar event occurs in Schottky-type junctions, where a semiconductor is in contact with a metal or an electrolytic solution [Figure 1].

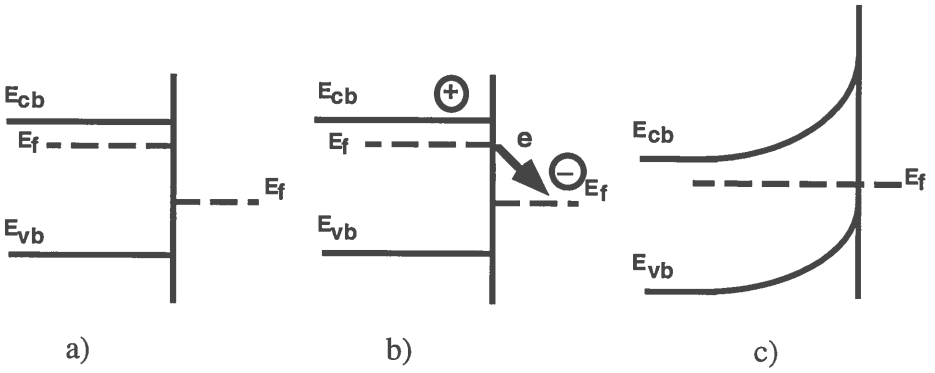

Figure 1. The formation of a Schottky-type barrier, a) n-type semiconductor and metal (or electrolyte) before junction formation, b) Immediately after junction formation electrons flow out of the semiconductor into the lower energy Fermi level of the metal, c) the equilibrium potential at the junction bends the condunction and valence bands.

The photoelectrochemical cell is based on a semiconductor-electrolyte Schottky-type junction [Figure 2a]. Such devices are easier to manufacture than the purely solid state cell but the instability of the semiconductor limits their practical use in photovoltaic arrays [7]. The photodecay of the semiconductor is related to the rate of charge capture by the intended agent in solution. The rate constant for the hererogeneous charge transfer (charge capture), by the Marcus/Gerischer theory, is dependent upon the reorganization energy for the donor and acceptor species and the diffusion of the solution species to the surface [8]. These factors, which limit the rate of the regeneration of the photoaccepting species, are important in all "wet" photovoltaic cells.

Like the photoelectrochemical cell, the photogalvanic cell is based on a solution-semiconductor contact. The major differences in the designs are 1) the electrolytic solution in the photoelectrochemical cell is replaced by a solvated photoactive dye and 2) the small band gap semiconductor is replaced with a wide band gap semiconductor, e.g. TiO_2, SnO_2, ZnO [9]. While photocorrosion of the semiconductor is no longer a major inconvenience, the efficiency of photogalvanic cells is severely limited by the inability of the excited molecule to diffuse to the semiconductor surface before undergoing radiative decay.

Recently, strides have been made in the development of a third type of "wet" photovoltaic cell [10], where colloidal TiO_2 (a wide band gap semiconductor) attached to a conducting surface (SnO_2:F) is sensitized to visible light by an adsorbed inorganic dye [11]. The most efficient dyes are derivatives of the *cis*-X_2(2,2'-bipyridyl-4,4'-dicarboxylate)$_2$M(II) dication (X = Cl, Br, I, CN, SCN; M = Ru, Os) [12]. These cells have displayed maximum efficiencies of 10% and incident-photon-to-current efficiencies greater than 90%.

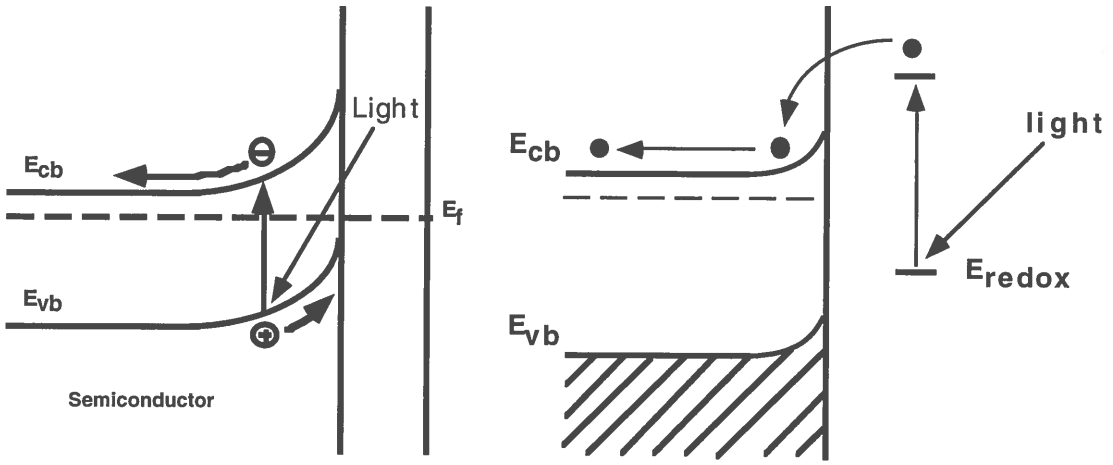

Figure 2. Separation of charges in different types of photovoltaic cells, a) light absorbtion by semiconductor and separation at a Schottky-type barrier (eg. "Dry" solar cells based on Schottky-type junctions or photoelectrochemical cells), b) light absorbtion by dye and dye-semiconductor charge separation (eg. photogalvanic cells or dye sensitized semiconductors).

The design of dye sensitized wide band gap photovoltaic cells resulted directly from the observed difficulties in other systems. The use of wide band gap semiconductors is advantageous due to their optical clarity and their resistance to photocorrosion. The design of meso-

porous films greatly increases the surface concentration of the absorbing dye and thereby increases the efficiency of light absorption for the cell. Finally, the adsorption of the photoactive dye on the semiconductor allows for rapid, direct injection of electrons into the surface [Figure 2b] and greatly reduces radiative decay, which is the principal disadvantage of photogalvanic cells. The desire to improve the efficiencies of dye sensitized cells has led to efforts focused on the derivitization of the dye by either ligand augmentation [13] or antenna functionalization [11b] and to investigations of the binding of the dye to the electrode surface [14].

References

1. U. S. Bureau of the Census, *Statistical Abstract of the United States: 1993*; 113th edition; Washington, D.C., 1993.

2. Halacy, D. "Solar Energy" In *Encyclopedia of Chemical Technology* ; Wiley: New York, 1983; Vol. 21, pp 294-342.

3. Memming, R. "Photoelectrochemical Solar Energy Conversion," *Top. Cur. Chem.* **1988**, *143*, 79-112.

4. Tribatsch, H. "Metal Sulfides in Photovoltaic, Photoelectrochemical and Solar Biological Energy Conversion," In *Studies in Inorganic Chemistry*; Muller, A., Krebs, B., Eds.; Elsevier: New York, 1984; Vol. 5, pp 277-310.

5. Araujo, G. L.; Marti, A. "Absolute Limiting Efficiencies for Photovoltaic Energy Conversion," *Sol. Energy Mat. Sol. Cells* **1994**, *33*, 213-240.

6. Bard, A. J. *Integrated Chemical Systems*; Wiley: New York, 1994; Chapter 6.

7. Fajardo, A. M.; Karp, C. D.; Kenyon, C. N.; Pomykal, K. E.; Shreve, G. A.; Tan, M. X.; Lewis, N. S. "New Approaches to Solar Energy Conversion Using Si/Liquid Junctions," *Sol. Energy Mat. Sol. Cells* **1995**, *38*, 279-303.

8. (a) Marcus, R. A. "Reorganization Free Energy for Electron Transfers at Liquid-Liquid and Dielectric Semiconductor-Liquid Interfaces," *J. Phys. Chem.* **1990**, *94*, 1050-1055.

   (b) Lewis, N. S. "Charge Transfer Rate Constants for Semiconductor/Liquid Contacts," *Sol. Energy Mat. Sol. Cells* **1995**, *38*, 323-325.

   (c) Pomykal, K. E.; Fajardo, A. M.; Lewis, N. S. "Stability of n-Si/CH_3OH Contacts as a Function of the Reoganization Energy of the Electron Donor," *J. Phys. Chem.* **1995**, *99*, 8302-8310.

9. Rabinowitch, E. "The Photogalvanic Effect: I. The Photochemical Properties of the Thionine-Iron System," *J. Chem. Phys.* **1940**, *8*, 551-559.

10. (a) Smestad, G.; Bignozzi, C.; Argazzi, R. "Testing of Dye Sensitized TiO_2 Solar Cells I: Experimantal Photocurrent Output and Conversion Efficiencies," *Sol. Energy Mat. Sol. Cells* **1994**, *32*, 259-272.

(b) Wrighton, M. S.; Ellis, A. B.; Wolczanski, P. T.; Morse, D. L.; Abrahamson, H. B.; Ginley, D. S. "Strontium Titanate Photoelectrodes. Efficient Photo-assisted Electrolysis of Water at Zero Applied Potential," *J. Am. Chem. Soc.* **1976**, *98*, 2774-2779.

(c) Liska, P.; Vlachopoulos, N.; Nazeeruddin, M. K.; Compte, P.; Gratzel, M. "*cis*-Diaquabis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) Sensitizes Wide Band Gap Oxide Semiconductors Very Efficiently over a Broad Spectrum in the Visible," *J. Am. Chem. Soc.* **1988**, *110*, 3686-3687.

11. (a) O'Regan, B.; Moser, J.; Anderson, M.; Gratzel, M. "Vectorial Electron Injection into Transparent Semiconductor Membranes and Electric Field Effects on the Dynamics of Light-Induced Charge Seperation," *J. Phys. Chem.* **1990**, *94,* 8720-8726.

(b) Amadelli, R.; Argazzi, R.; Bignozzi, C. A.; Scandola, F. "Design of Antenna-Sensitizer Polynuclear Complexes. Sensitization of Titanium Dioxide with $[Ru(bpy)_2(CN)_2Ru(bpy(COO)_2)_2^{2-}$," *J. Am. Chem. Soc.* **1990**, *112,* 7099-7103.

(c) O'Regan, B.; Gratzel, M. "A Low-Cost, High-Efficiency Solar Cell Based on Dye-Sensitized Colloidal TiO_2 Films," *Nature* **1991**, *353*, 737-740.

12. (a) Heimer, T. A.; Bignozzi, C. A.; Meyer, G. J. "Molecular Level Photovoltaics: The Electooptical Properties of Metal Cyanide Complexes Anchored to Titanium Dioxide," *J. Phys. Chem.* **1993**, *97*, 11987-11994.

(b) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Muller, E.; Liska, P.; Vlachopoulos, N.; Gratzel, M. "Conversion of Light to Electricity by *cis*-X_2Bis(2,2'-bipyridyl-4,4'-dicarboxylate)ruthenium(II) Charge-Transfer Sensitizers (X = $Cl+^-$, Br^-, I^-, CN^-, and SCN^-) on Nanocrystalline TiO_2 Electrodes," *J. Am. Chem. Soc.* **1993**, *115*, 6382-6390.

13. (a) Bignozzi, C. A.; Argazzi, R.; Schoonover, J. R.; Meyer, G. J.; Scandola, F. "Photosensitization of Wide Bandgap Semiconductors with Antenna Molecules," *Sol. Energy Mat. Sol. Cells* **1995**, *38*, 187-198.

(b) Argazzi, R.; Bignozzi, C. A.; Heimer, T. A.; Castellano, F. N.; Meyer, G. J. "Enhanced Spectral Sensitivity from Ruthenium(II) Polypyridyl Based Photovoltaic Devices," *Inorg. Chem.* **1994**, *33*, 5741-5749.

14. (a) Meyer, T. J.; Meyer, G. J; Pfenning, B. W.; Schoonover, J. R.; Timpson, C. J.; Wall, J. F.; Kobusch, C.; Chen, X.; Peck, B. M.; Wall, C. G.; Ou, W.; Erickson, B. W.; Bignozzi, C. A. "Molecular-Level Electron Transfer and Excited State Assemblies on Surfaces of Metal Oxides and Glass," *Inorg. Chem.* **1994**, *33*, 3952-3964.

(b) Bedja, I.; Hotchandani, S.; Kamat, P. V. "Preparation and Photoelectrochemical Characterization of Thin SnO_2 Nanocrystalline Semiconductor Films and Their Sensitization with Bis(2,2'-bipyridine)(2,2'-bipyridine-4,4'-dicarboxylic acid)ruthenium(II) Complex," *J. Phys. Chem.* **1994**, *98*, 4133-4140.