

# This Week's Citation Classic®

**Gerischer H.** Electrochemical photo and solar cells: principles and some experiments. *J. Electroanal. Chem. Interfac.* 58:263-74, 1975.  
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The photovoltages and photocurrents in photoelectrochemical cells are generated in Schottky barriers formed at the contact between a semiconductor and a redox electrolyte. A simple cell design was described and the relation to solid-state photovoltaic cells was analyzed. The specific problems of the electrochemical systems with respect to efficiency and stability were outlined. [The *SCI*® indicates that this paper has been cited in more than 365 publications.]

## Electrochemical Solar Cells Are Schottky Barrier Devices

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This paper was stimulated by a publication of A. Fujishima and K. Honda,<sup>1</sup> in 1972, who had achieved photodecomposition of water by illumination of TiO<sub>2</sub> electrodes with solar light. A year later, the first energy crisis created worldwide interest in alternative energy sources. Photoelectrolytic splitting of water has a close analogy to photosynthesis, with the important difference being that the energy carrier is hydrogen instead of carbohydrates, but the energy gained is nearly the same. This avoids the enormous difficulty of the reduction of CO<sub>2</sub>, which nature has achieved at room temperature with great perfection, while all technical processes for CO<sub>2</sub> reduction require a large input of additional free energy.

At that time, I had been studying photoelectrochemical processes at semiconductor electrodes for more than 10 years, with emphasis on the kinetics of the charge transfer reaction at the interface to an electrolyte. This provided me with a clear understanding of the conditions that were required to generate photocurrents. In the kinetic experiments, these conditions were controlled externally. With this experience, however, it was not difficult to analyze the function of an electrochemical cell with a semicon-

ductor electrode and an inert counter electrode, both in contact with the same redox electrolyte, as a source of photoelectric energy.

In this paper, a simple cell design was described and tested with n-type semiconductors by measuring photovoltages at open circuit and photocurrents at closed circuit. I used the semiconductors CdS, CdSe, and GaP, which absorb visible light and could therefore reach much higher efficiencies under solar illumination than TiO<sub>2</sub>, which absorbs only in the ultraviolet range. The theoretical analysis showed that the existence of a depletion layer at the semiconductor/electrolyte contact is necessary for the generation of photocurrents and photovoltages. This requires a suitable combination of a semiconductor and a redox system in order to form such a depletion layer at equilibrium. The photoelectrochemical cell is in its function fully equivalent to a semiconductor/metal cell with a Schottky barrier, with the same conversion efficiency limitations.

In the discussion of this paper, some advantages due to the variability of the combination of semiconductors and redox systems and the simplicity of the contact formation were emphasized. However, serious disadvantages also were pointed out, particularly the energy losses by slow electron transfer rates at the semiconductor electrode and the susceptibility of semiconductors in contact with electrolytes to photodecomposition.

The potential and the problems of photoelectrochemical solar cells were later analyzed much more extensively in two review papers.<sup>2,3</sup>

Many systems have been investigated since, making considerable improvements with respect to energy conversion efficiency and stability.<sup>4,5</sup> But the efficiency and lifetime of solid-state devices have not yet been reached. I think the merit of this paper was that it gave a first clear idea of the function of photoelectrochemical cells. It also indicated their weaknesses, however. This has not delighted all of my colleagues.

1. Fujishima A & Honda K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* 238:37, 1972. (Cited 600 times.)
2. Gerischer H. Power generation by photoelectrolysis. (Bolton J R, ed.) *Solar power and fuels*. New York: Academic Press, 1977. p. 77-112. (Cited 50 times.)
3. . . . . Solar photoelectrolysis with semiconductor electrodes. (Seraphin B O, ed.) *Topics in applied physics*. Berlin, Federal Republic of Germany: Springer, 1979. Vol. 31. p. 115-72. (Cited 155 times.)
4. Semiconductor electrodes and their interaction with light. (Schiavello M, ed.) *Photoelectrochemistry, photocatalysis and photoreactors*. Dordrecht, The Netherlands: Reidel, 1985. p. 39-106.
5. Memming R. Photoelectrochemical solar energy conversion. (Steckhan E, ed.) *Topics in current chemistry*. Berlin, Federal Republic of Germany: Springer, 1988. Vol. 143. p. 79-112. (Cited 10 times.)