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Gerischer H. On the stability of semiconductor electrodes against photodecomposition.

J. Electroanal. Chem. Interfac. 82:133-43, 1977.

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Experiments demonstrated that the decomposition of semiconductors in contact with electrolytes by anodic oxidation depended on the availability of holes, and decomposition by cathodic reduction depended on the presence of electrons at the interface. The critical free energies of holes or electrons necessary to induce decomposition were derived in this paper from thermodynamic data. In the case of photodecomposition, the required charge carriers are the minorities being generated by light absorption. Their critical concentration was defined by their quasi-Fermi level in relation to the energy position of the band edges. [The *SCI*® indicates that this paper has been cited in more than 240 publications.]

Photodecomposition of Semiconductors— A Thermodynamic Approach

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It was in a solid-state physics seminar at the University of Stuttgart in 1956 that I heard a report of a paper from the Bell Telephone Laboratories (W.H. Brattain and C.G.B. Garrett¹) that described the very different behavior of p- and n-type germanium in contact with electrolytes under anodic and cathodic bias. I realized that a new type of electrochemical process occurred at such interfaces.

Having been trained as a physical chemist, my understanding of solid-state physics was very limited. It was, however, obvious to me that the electronic properties of the solid were a key issue for a deeper understanding of electrode reactions in contact with electrolytes. The results with germanium electrodes indicated that semiconductors opened a way to experimentally investigating the influence of the electronic properties on such processes. In contrast to metal electrodes, semiconductors offered at least two different types of electrons that could act as reaction partners—those of the conduction band or those of the valence band.

In this period, I was fortunate to work in an institute where the study and theory of the solid

state was the main objective (the Max-Planck-Institute of Metals, Stuttgart). I was exposed to solid-state theory rather unintentionally and tried to learn as much as possible. Thanks to the generosity of a colleague in physics (K. Seiler), who worked in the industry but was lecturing at the university, I received some germanium crystals and started some experiments together with a coworker. The outcome was very promising and gave a detailed kinetic analysis of the role of holes for the decomposition of semiconductors.² Later experiments led to the formulation of a general kinetic mechanism of the decomposition reactions.³

In the paper under review here, another generalization was made. It was the question of how the individual properties of different semiconductors control decomposition in particular electrolytes. An analysis was made by calculating, from thermodynamic data, redox potentials for the respective electrode reactions leading to decomposition. Although the equilibrium assumption involved in a thermodynamic approach is unrealistic, it gives the critical values of the redox potentials of electrons or holes (equivalent to their Fermi level) that have to be exceeded to make decomposition possible. For the case of photodecomposition, the redox potentials of the minority carriers in the semiconductors were characterized by their quasi-Fermi levels. Since Fermi levels are related to the energy position of the band edges, a classification of individual semiconductors could be given with respect to their stability.

The thermodynamics of anodic decomposition of semiconductors was independently analyzed in the same year by A.J. Bard and M.S. Wrighton,⁴ not dealing, however, with cathodic or photodecomposition. In a consecutive paper, the role of slow kinetics, which can improve the stability in comparison with the thermodynamic limits, was outlined.⁵ The model developed in these papers is generally used today in the discussion of stability questions (e.g., reference 6), although the origin is not always cited.

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2. Beck F & Gerischer H. Zum Mechanismus der anodischen Auflösung von Germanium in alkalischer Lösung. *Ber. Bunsen Ges. Phys. Chem.* 63:500-10, 1959.
3. Gerischer H & Mindt W. The mechanisms of the decomposition of semiconductors by electrochemical oxidation and reduction. *Electrochim. Acta* 13:1329-41, 1968.
4. Bard A J & Wrighton M S. Thermodynamic potential for the anodic dissolution of n-type semiconductors. *J. Electrochem. Soc.* 124:1706-10, 1977.
5. Gerischer H. Electrolytic decomposition and photo-decomposition of compound semiconductors in contact with electrolytes. *J. Vac. Sci. Technol.* 15:1422-8, 1978.
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