Semiconductor Electrodes

XXXV. Slurry Electrodes Based on Semiconductor Powder Suspensions

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Irradiated suspensions of semiconductor powders, e.g., TiO_2, have been employed in such heterogeneous photo processes as the oxidation of cyanide, the decomposition of carboxylic acids, and the deposition of metals. Details about these and other reactions are given in recent reviews (1-3). The mechanism proposed for these processes is based on the formation of an electron-hole (e^-h^+) pair at the particle surface upon absorption of light of energy greater than the semiconductor band-gap. The particle then behaves as a short-circuited cell with both oxidation and reduction taking place at the particle surface. Recent measurements of the electrophoretic mobility of TiO_2 powder have demonstrated that in solution, the surface charge on the particle under illumination is more negative than that measured in the dark (4). Moreover, this negative charge persists for at least 10-15 minutes after the irradiation stops. These results suggest that when the holes are scavenged by an oxidation process, electron density builds up on the particle surface. We report here that this excess charge can be collected on an inert electrode to produce an anodic current flow. Thus, semiconductor powder suspensions (e.g., TiO_2, WO_3, CdS) can behave as electrodes ("slurry electrodes") in the same manner as the single crystal and polycrystalline semiconductor materials currently being investigated. Measurements involving such slurry electrodes are of use not only for the characterization of the powders but may also have practical applications in photoelectrochemical cells.

In a typical experiment, a suspension of n-TiO_2 particles in 0.02 M HCl was deaerated for 24 hours prior to measurements. A Pt foil (area ∿ 3 cm^2), polished with Al_2O_3 and cleaned in boiling HNO_3, was used as the collector electrode. Electrochemical measurements were conducted in a Pyrex H-cell, with the compartments separated by a fine-porosity glass frit. One compartment contained the deaerated TiO_2 suspension while the other compartment contained a Pt counter electrode and 0.02 M HCl with a low oxygen concentration to support a current flow. A 2500 W xenon lamp, operated at 1600 W, was used for illumination. A Pyrex water bath approximately 15 cm in diameter was placed in front of the electrochemical cell to remove IR radiation.

A negligible current flowed between the two half-cells in the dark under short circuit conditions. When the TiO_2 suspension was irradiated, a cathodic current transient appeared; the current quickly became anodic and finally attained a steady anodic current

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level (Fig. 1b). When the light beam was interrupted, an anodic transient appeared and the anodic current decayed to zero. In a control experiment in the absence of the suspension under otherwise identical conditions, only very small current responses appeared under illumination (Fig. 1a). The behavior of the TiO_2 suspension can be interpreted based on the model for photoprocesses at the particle surface (Fig. 2). The photoproduced hole rapidly forms a hydroxl radical that reacts in a following reaction to produce oxygen (5). In the absence of oxidants in solution, electrons accumulate at the powder surface. While proton reduction is a possible process, this reaction is apparently slow at an uncatalyzed TiO_2 surface. The direction of current flow depends upon the relative rates of electron transfer between the collector electrode and the particle. Initially a cathodic current, probably representing reduction of OH•, is observed. However the accumulation of electrons and the subsequent reaction of •OH leads to a net anodic current. A quantitative treatment of the model of Fig. 2, to be described elsewhere, leads to current-time (i-t) curves resembling the experimental ones. Evidence in favor of such a model is the finding that addition of oxygen to the suspension quenches the anodic photocurrent, and produces only a brief cathodic transient and a small cathodic steady state current, since the photogenerated electrons react with O_2. Similarly the anodic current with platinized TiO_2 is much smaller, because Pt catalyzes the proton reduction reaction. Finally the addition of acetate causes a decrease or elimination of the cathodic transient and an increase in the anodic current, because the preferential oxidation of acetate at the powder produces methyl radical which undergoes a very rapid reaction (6), so that electron transfer to this species does not occur.

Similar behavior is observed with other semiconductor powders. The i-t curves with WO_3 powder in sulfate solutions (pH 1.8) are similar to those of TiO_2 (Fig. 1c). For a CdS suspension in a sulfate medium, however, no cathodic transient is observed and the current rises in an anodic direction and then decays to a steady value (Fig. 1d). In this case the photogenerated holes lead to decomposition of the semiconductor

$$CdS + 2h^+ \rightarrow Cd^{2+} + S \qquad [1]$$

and the sulfur so produced is not reducible. The addition of Na_2SO_3 (10^{-5} M) which retards this decomposition reaction (8) caused no significant change in the photoresponse.

Electrochemical studies of semiconductor slurries in the dark and under illumination appear promising. The determination of photocurrent as a function of the wavelength of the irradiating light can provide information about the band gap energy and, perhaps the existence of energy levels within the gap, with the powder immersed in the reaction medium. Moreover the effect of solution conditions on the photoresponse can provide information about relative reaction rates at the particle surface. Although the magnitudes of the photocurrents generated with the slurry electrodes are small compared to single crystal and some polycrystalline film electrodes under similar irradiation intensities, they may find some practical application. They are potentially very inexpensive and easy to construct and replace. Regenerative (photovoltaic) and storage (photoelectrosynthetic) cells employing slurry electrodes are possible and are currently under investigation in this laboratory.

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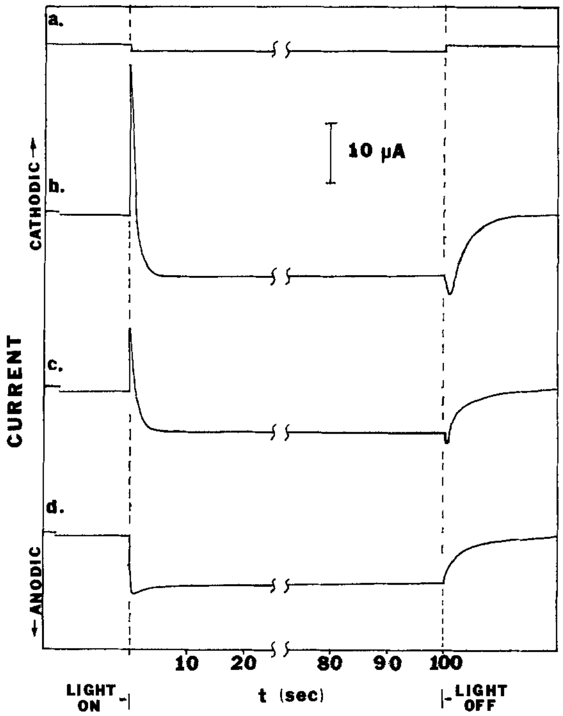

Fig. 1. Current-time responses under and following irradiation with xenon lamp. (a) Pt electrode alone in 0.02 M HCl; (b) suspension of 25 mg TiO_2 in 40 ml 0.02 M HCl; (c) 25 mg WO_3 in 40 ml 6.7 mM Na_2SO_4 (pH 1.8); (d) 30 mg CdS in 40 ml 6.7 mM Na_2SO_4 (pH 5).

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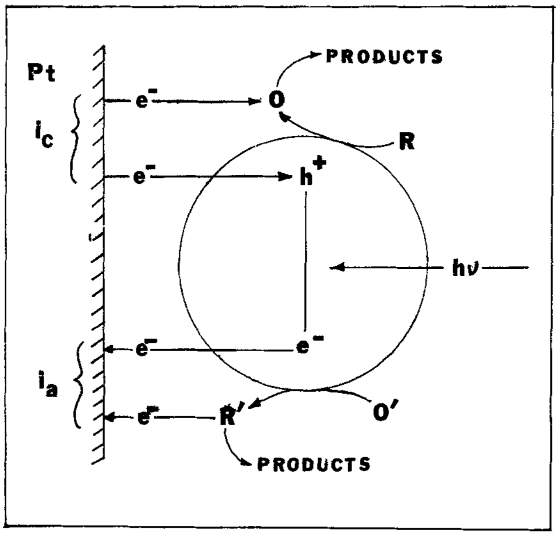

Fig. 2. Model of process at particle surface. R represents a solution reductant (e.g. H_2O, $CH_3CO_2^-$) and O' a solution oxidant (e.g. O_2).

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