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Photopotential Behavior of Platinized TiO₂ Particles

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posites, made by the process described here and reported by one of the authors in a separate paper (4), appears to approach that of pure lead. Initial deep cycling experiments of battery cells made with small FP/Pb composite grids indicate that grid growth is negligible compared with unreinforced pure lead grids.

Fabrication of larger scale FP/Pb composite grids and demonstrations of their performance in battery cells is underway. Deep cycling tests with small FP/Pb grids are continuing in order to determine eventual failure mechanisms.

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Photopotential Behavior of Platinized TiO₂ Particles

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The photocatalytic generation of hydrogen from water is one of the attractive means of the conversion of solar energy into chemical energy (1-3). Pt/SrTiO₃ (1) and Pt/TiO₂ (2) were shown to be able to decompose water photocatalytically. Photocatalysts dispersed in the liquid phase are considered to behave as short-circuited photoelectrochemical cells (4), and we have demonstrated that the measurement of the potential of suspended catalysts provides useful information concerning their reaction mechanism (5). Recently Dunn *et al.* reported the usefulness of electrochemical measurements in the characterization of suspended photocatalysts (6, 7).

To provide further information on the mechanism of photocatalytic decomposition of water on these catalysts, we report here the photoeffect on the potential of platinized catalysts suspended in NaOH solution.

The platinized TiO₂ catalysts (2 weight percent Pt) were prepared by impregnating TiO₂ (anatase) with H₂PtCl₆ solutions (8). The impregnates were dried in air at 110°-120°C for 16 hr and then reduced in hydrogen at 300°C for 2 hr. The catalysts (0.2g) were suspended in 70 ml of 1N NaOH solution in a cell with main and reference compartments separated by a Luggin capillary and a stopcock. A quartz window was mounted on the main compartment. A gold-plated platinum wire and an Ag/AgCl electrode were used as a measuring probe (9) and a reference electrode, respectively. A 500W xenon lamp with a monochromator (Ritsu Oyo Kogaku) was used as a light source. Illuminating the probe electrode was avoided. Purified helium gas was passed through the solution for 30 min prior to the measurement. During the measurement, the catalyst-containing solution was stirred magnetically.

The potential-time relation of the catalysts under pulsed illumination of 360 nm monochromatic light is shown in Fig. 1. The potential shifted negatively under illumination and reached some steady value, according to

$$E(t) = E(0) + \Delta E_{st}(1 - e^{-t/\tau}) \quad [1]$$

where $E(t)$ and $E(0)$ are the potentials at time t and

in dark, respectively, ΔE_{st} is the difference between the potential in dark and the steady potential, and τ is the time constant (~ 30 sec for this process). After the interruption of light, the potential returns to the original value, $E(0)$, by

$$E(t') = \Delta E_{st} e^{-t'/\tau} \quad [2]$$

where t' is the time after the interruption of light and

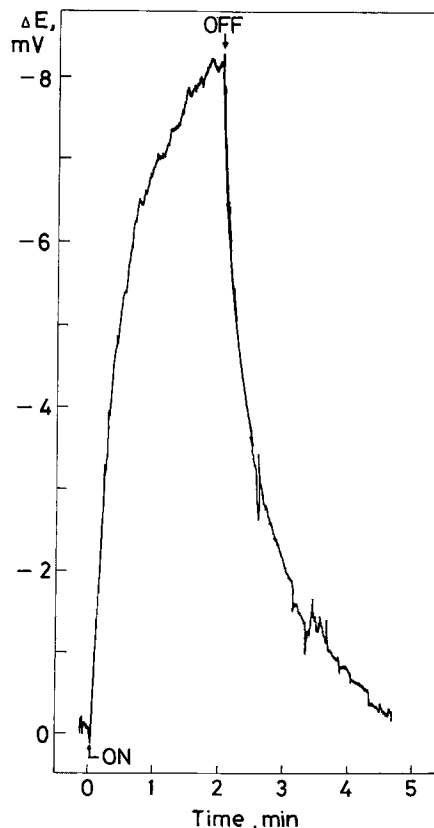
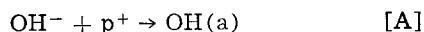


Fig. 1. The potential-time relation of Pt/TiO₂ catalyst in 1N NaOH under pulsed illumination of 360 nm monochromatic light.

* Electrochemical Society Active Member.

Key words: photocatalyst, semiconductor, titanium dioxide.

τ is the time constant (~ 45 sec for this process¹). The wavelength dependence of ΔE_{st} shown in Fig. 2 clearly indicates that the photoeffect on the catalyst potential is created by the absorption of light by TiO_2 ($E_g = 3$ eV). This effect will be explained by considering the band structure of Pt/ TiO_2 catalyst shown in Fig. 3. This is based on a model that considers Pt and TiO_2 electrodes at short circuit. In the dark, the bands of TiO_2 bend up toward $\text{TiO}_2/\text{electrolyte}$ and TiO_2/Pt interfaces. When the catalysts are illuminated by the bandgap light, hole-electron pairs are formed. Due to the band-bending, the holes and the electrons move toward the $\text{TiO}_2/\text{electrolyte}$ interface and the interior of TiO_2 , respectively. The holes at the $\text{TiO}_2/\text{electrolyte}$ interface tend to react with OH^-



while the electrons are unable to react with water because the Fermi level of the catalysts is not high enough. Thus the Fermi level of the catalysts rises, i.e., the potential becomes more negative so that the rate

¹ Preliminary experiments show that the time constant of the decay of photopotential of sintered Pt/ TiO_2 electrode is considerably larger (~ 20 min) than that of this process.

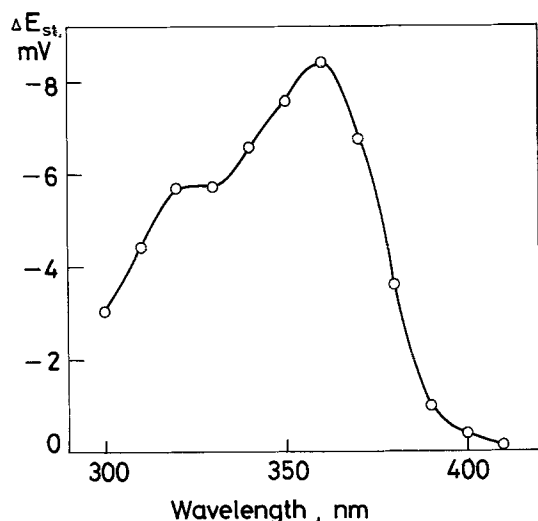


Fig. 2. The effect of the wavelength of the light on ΔE_{st} . The values of ΔE_{st} are not calibrated for the photon numbers.

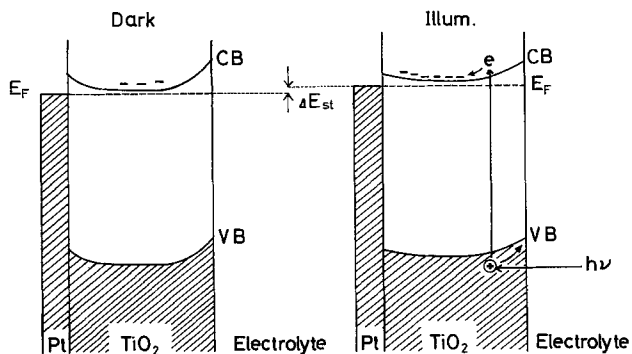
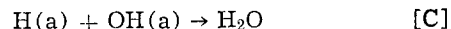


Fig. 3. The band structure of Pt/ TiO_2 catalyst in (a) dark and (b) under illumination. CB and VB are the conduction and valence band, respectively, and E_F is the Fermi level.

of electron consumption by reaction [B] at the Pt surface becomes equal to the hole consumption rate



When the potential becomes more negative, the degree of band-bending in TiO_2 becomes smaller and the electron-hole recombination rate increases. Reaction [C], which can be considered as the hole-electron recombination via adsorbed states, is also accelerated when the potential becomes negative



Thus the potential does not exceed some steady value at which the rate of electron excitation is equal to that of electron consumption by the reaction with H_2O and the recombination. In this system, the steady potential is positive compared with the reversible hydrogen electrode potential, suggesting no hydrogen evolution at an atmospheric pressure.

When the illumination is interrupted, the electron-hole pairs are no longer generated and the adsorbed hydrogen atoms are consumed by reaction [C] and the back-reaction of reaction [A]. Thus the potential returns to the original value. The relatively short time constant of this process compared with the time constants of the decay of photostimulated emf at a platinum coated with pigmentary TiO_2 (10) and at a sintered Pt/ TiO_2 electrode, suggests that the reaction [C] is responsible for the quick return of the potential to the original value in this process.

In summary, we have demonstrated that the measurements of the potential of photocatalysts provide useful information on the mechanism of the photocatalytic water decomposition reaction.

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