Sintered ZnO Electrode for Dye-sensitized Photocell

Michio MATSUMURA, Shigeyuki MATSUDAIRA, Hiroshi TSUBOMURA, Masasuke TAKATA* and Hiroaki YANAGIDA*

(*Faculty of Engineering Science, Osaka University, Toyonaka-shi 560
*Department of Industrial Chemistry, Faculty of Engineering, University of Tokyo 113)

[Received November 22, 1978]

Key-words: Dye-sensitization, Dye-sensitized photocurrent, Photocell, Zinc oxide, Sintered zinc oxide electrode

The electrochemical system \( \langle n\text{-type semiconductor electrode} \mid \text{aqueous solution of electrolyte} \mid \text{platinum electrode} \rangle \) has widely been investigated as a photocell utilizing the solar energy\(^{1-3}\). When the n-type semiconductor is anodically polarized, an induced electrical
current is obtained by the irradiation of light whose photon energy is greater than $E_g$, the band gap of the semiconductor. The light with its photon energy less than $E_g$, however, can give rise to the dye-sensitized photocurrents if a proper dye is adsorbed on the surface of the semiconductor electrode\textsuperscript{2), 4, 8).}

In the present communication, the effect of the microstructure of the semiconductor electrode upon the dye-sensitized photocurrent was investigated using ZnO electrode of various degree of sintering.

A slurry was made of ZnO powders (99.99 % pure) kneaded with an aqueous solution of desired concentration of Al(NO$_3$)$_3$·9H$_2$O. The slurry was dried with an i.r. lamp, ground in an agate mortar, calcined in air at 630°C for 6 h, and ground again in an agate mortar. The particles thus obtained (particle size 0.03 to 0.4 μm) were pressed into pellets, 10 mm in diameter and 2 mm thick, under a pressure of 10 kg/cm$^2$ (no binder used). The pressed bodies were heated in air at temperatures from 900 to 1300°C for 5 h to sinter the particles and cooled to room temperature in the furnace.

One of the face of the sintered ZnO pellet was coated with indium to make an ohmic contact. A piece of copper lead wire was attached to the contact with silver paste. The structure of the electrode was almost the same as that described previously\textsuperscript{9), 10). Before measurement, the electrode was polished with silicon carbide abrasive, etched with hydrochloric acid, washed with water and dried.

The potential of the semiconductor electrode vs. the reference electrode (SCE) was controlled by Hokutodenko HA-101 potentiostat and the current was measured with Yokogawa-Hewlett-Packard 4304 B electrometer. A xenon lamp of Ushio Electric, Inc. (500 W) was used as the light source. The light was monochromatized by Japan Jarrell-Ash 0.25 m Ebert type monochromator. The solution consisted of 0.2 M KNO$_3$ (supporting electrolyte), 1×10$^{-4}$M Rose Bengal (dye) and 1×10$^{-3}$M hydroquinone (reducing agent). High purity nitrogen gas was bubbled through the solutions before measurement to remove oxygen gas from the cell. After measurement, sintered ZnO pellets colored more deeply red with decreasing the degree of sintering, indicating adsorption of dye.

Figs. 1 and 2 show the characteristics of dye-sensitized photocurrent vs. degree of sintering for ZnO electrode doped with 0.5 mol% Al$_2$O$_3$ and 2.0 mol% Al$_2$O$_3$, respectively. The addition of Al$_2$O$_3$ is known to suppress the sintering rate of ZnO due to the decrease in concentration of interstitial zinc ions by the incorporation of Al ions\textsuperscript{11).}

As shown in Figs. 1 and 2, the dye-sensitized photocurrent becomes maximum at an intermediate degree of sintering. The photocurrent was small for well sintered bodies
because of a small amount of adsorbed dye on the smooth surface. Also the current was small for poorly sintered bodies since the inner resistance was high\(^1\). Properly sintered bodies have enough surface area to adsorb a large amount of active dye and have enough conductivity.

The highest value of the apparent quantum yield of the photocurrent, defined as the number of flowing electrons divided by the number of incident photons on the electrode, reached ca. 22\% for the ZnO electrode doped with 1.0 mol\% Al\(_2\)O\(_3\) (the degree of sintering; 55\%).

From the above results, it was shown that the properly sintered zinc oxide electrode with desired porosity was more efficient for dye-sensitized photoelectrode than well sintered one.

References
1) A. Fujishima and K. Honda, Nature, 238, 37-38