Photoelectrochemical Properties of $CdSnO_3$ and $LaRhO_3$ Electrodes in Aqueous Solutions

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$CdSnO_3$ sinter electrodes work as n-type photoanodes with a high electrochemical stability in alkaline solutions. A thin film $LaRhO_3$ electrode prepared on a substrate platinum plate shows p-type photoresponse in aqueous solutions, giving rise to the hydrogen evolution with a fair stability. The threshold wavelength beyond which no photoresponse appears is *ca.* 700 nm for the former and 950 nm for the latter electrode.

The photovoltaic effect that appears on illumination of semiconductor electrodes immersed in electrolytes can be utilized to convert solar energy into either electricity or chemical substances, or the both in photoelectrochemical cells or heterogeneous chemical reaction systems.[1–8] The stability of semiconductors is essential in these applications, but most of semiconductor materials are unstable in aqueous solutions, suffering either anodic decomposition or the cathodic decomposition or the both.[9] Although a principle for stabilizing unstable semiconductor electrodes has been proposed,[10,11] semiconductors of high electrochemical stability are still desirable for elimination of any corrosion problem of photoelectrodes.

Until now several n-type semiconducting oxides have been found to possess high stabilities under anodic bias,[3,4] but searches for another stable materials are still important in the following two respects. (1) Through such investigations, a material of high electrochemical stability and negative flat-band potentials, which are essential for photoanodes in water photolysis cell,[1] may be found. (2) Besides photoelectrodes in photoelectrochemical cells, semiconductors are useful as photocatalysts. Studies in this area are steadily growing. In order to find an efficient heterogeneous reaction system using photocatalysts, investigations on the activity of photocatalysts for an objective reaction are desirable to be done for as many photocatalysts as possible, because the prediction of the activity of photocatalysts is impossible to be done in the present status. The kind of stable semiconductors is quite limited and not much enough to satisfy such requirements. By these reasons, we have been investigating photoelectrochemical properties of a variety of oxides. This paper describes our findings obtained by the investigations with such purposes.

We have found that $CdSnO_3$ having the n-type conductivity shows a high electrochemical stability with a large photoresponse which is comparable to α-Fe_2O_3, although a result showing the photoresponse has recently been reported.[12] Besides this material, we have observed that a $LaRhO_3$ thin film prepared on a substrate platinum plate shows a fairly stable p-type photoresponse in aqueous solutions. It has already been reported from studies in solid states that both $CdSnO_3$[13] and $LaRhO_3$[14] possess semiconductivity, but no conductivity type has been reported. As for the former material, however, the n-type conductivity is suggested from the finding[12] that it shows the photoresponse under anodic bias. To our knowledges, no optical properties of $CdSnO_3$ and $LaRhO_3$ have been investigated to date.

Electrochemical stabilities of these materials cannot be predicted in advance. In order to do this, we need knowledges on flat-band potentials and energy gaps of these materials.[10,11] The flat-band potentials can in principle be estimated by combining the energy gap value and the bulk electronegativity of the material[15,16] which is calculated by employing the Nethercot's hypothesis.[17] The lack of knowledge on the energy gap of $CdSnO_3$ and $LaRhO_3$, however, makes it impossible to take such an approach. In the present study, therefore, basic properties has been obtained.

Experimental

The preparation of $CdSnO_3$ was made in a manner similar to that reported by Smith.[18] Reagent grade CdO and SnO_2 powders in a molar ratio 1 : 1 were mixed in an agate mortar, and pressed into 13 mm diameter and 1 mm thickness. The pressed disc was then fired at 1000 °C for 6 h in air. According to X-ray diffraction patterns of the prepared oxide, it consisted of a $CdSnO_3$ single phase. The prepared oxide sinter was then subjected to water proofing in the following manner. The sinter was immersed in 1% polystyrene in benzene, and evacuation was made until no gas bubble was evolved from the sinter surface, followed by heating up to 100 °C to evaporate benzene. After repeating such water-proofing procedures several times, the surface of the sinter was gently polished with #2000 emery papers to remove off surface-covered polystyrene. Indium was then evaporated onto the one end face and an electrical lead wire was attached there. Finally, the sinter was mounted in a glass tube with epoxy resin to serve as an electrode.

$LaRhO_3$ was prepared on a substrate Pt plate. The Pt plate was polished with #1500 emery papers, followed by immersion in aqua regia. After boiling in a mixed solution of NaOH and Na_2CO_3 as a defatting procedure, it was washed with de-ionized water. 0.1 $mol \cdot dm^{-3}$ solutions of $LaCl_3 \cdot 7H_2O$ and $RhCl_3 \cdot 3H_2O$ were mixed with the same volume, and the mixed solution was applied to one side of the Pt plate in five successive coatings to give 1.2×10^{-5} mol of metal/cm^2. After each coating, the solution was dried at *ca.* 100 °C in a drying oven. The sample was then pre-heated at 480 °C for 1 h to decompose the chlorides, followed by firing at 1100 °C for 34 h in air. X-Ray diffraction peaks of the prepared sample were composed of reported diffraction peaks of Pt and $LaRhO_3$.[19] The back face and edge portions of the substrate Pt were coated with silicone adhesive(Silicone Sealant, Shinetsu Chemicals) to serve as an electrode.

Polarization measurements were carried out by using a Nikko Keisoku model DPGS-1 potentiogalvanostat. A 500 W super high pressure mercury arc lamp was used as a light source except where measurements of action spectra of photocurrents were carried out. The action spectra were obtained with monochromatic light which was obtained by using a 500 W xenon lamp as a light source and a grating monochrometer (JASCO, model CT-25), and were not corrected for the intensity variation of the lamp-monochrometer output. Electrode capacitance *vs.* potential relations were obtained by using the bridge method as described previously.[20]

Results and Discussion

Photoelectrochemical Properties of $CdSnO_3$ Electrodes. The resistivity of the prepared samples was in a range between 1 and 10 Ω cm, as determined by the four probe method. Figure 1 shows steady state current-potential curves of the prepared electrode in 1 mol·dm^{-3} NaOH and 0.5 mol·dm^{-3} H_2SO_4. Also given in this figure are current-potential curves obtained with illumination of chopped light at 2 Hz in a mixed solution of 0.5 mol·dm^{-3} acetic acid and 0.5 mol·dm^{-3} sodium acetate. It is seen in this figure that the onset potential of the anodic photocurrents shifts towards the negative direction with a decrease in acidity, as usually observed at other oxide semiconductor electrodes.

Shottky-Mott plots of electrode capacitance *vs.* potential relations are given in Fig. 2. Although a large frequency dispersion is observed in the plots, the potentials which are obtained by extrapolating $1/C^2$ to the potential axis are in good agreements with each other between 1 and 5 kHz. Therefore, the flat-band potential determined by such plots, which is *ca.* 0.3 V *vs.* SCE in 0.5 mol·dm^{-3} H_2SO_4 and *ca.* −0.4 V *vs.* SCE in 1 mol·dm^{-3} NaOH, is of significance. The onset potential of the anodic photocurrents, given in Fig. 1, is in rough accord with the determined flat-band potentials.

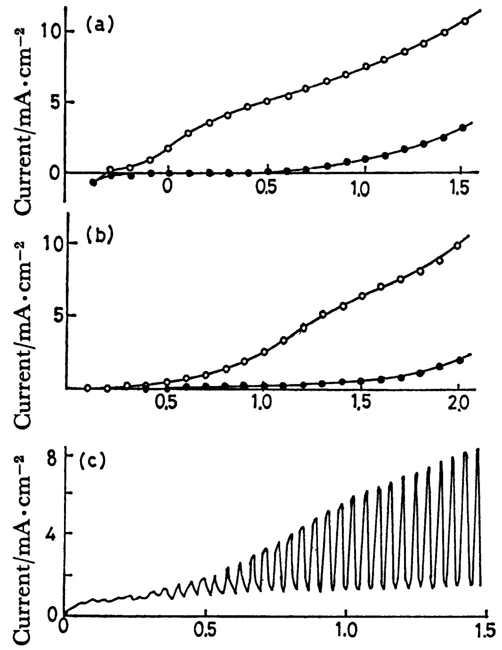

Fig. 1. Current-potential curves of $CdSnO_3$ electrode in (a) 1 mol·dm^{-3} NaOH and (b) 0.5 mol·dm^{-3} H_2SO_4 under steady state conditions, and (c) 0.5 mol·dm^{-3} acetic acid + 0.5 mol·dm^{-3} sodium acetate with illumination of chopped light at 2 Hz.
○: Under illumination, ●: in the dark.

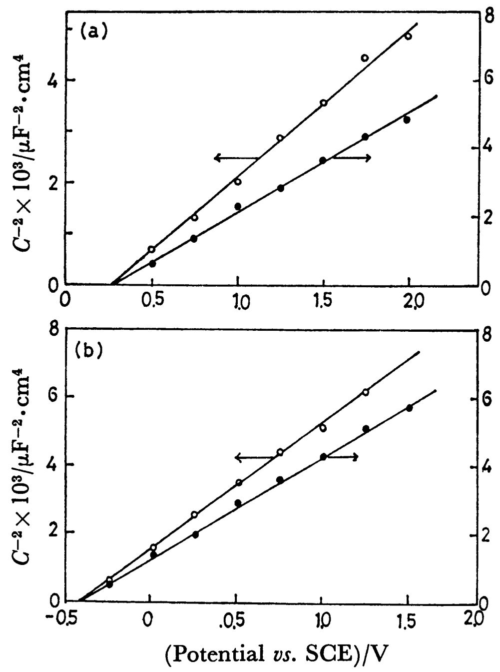

Fig. 2. Schottky-Mott plots of electrode capacitance *vs.* potential relations in (a) 0.5 mol·dm^{-3} H_2SO_4 and (b) 1 mol·dm^{-3} NaOH.
Frequency chosen; ○: 1 kHz, ●: 5 kHz.

By anodic polarization in 0.5 mol·dm^{-3} H_2SO_4, the electrode surface was gradually changed from yellow to white, suggesting that the electrode is unstable in acidic solutions. X-Ray diffraction patterns of the color-changed surface showed the existence of SnO_2. Similar observations have recently been reported for Cd_2SnO_4 electrodes.[21,22] In alkaline solutions, however,

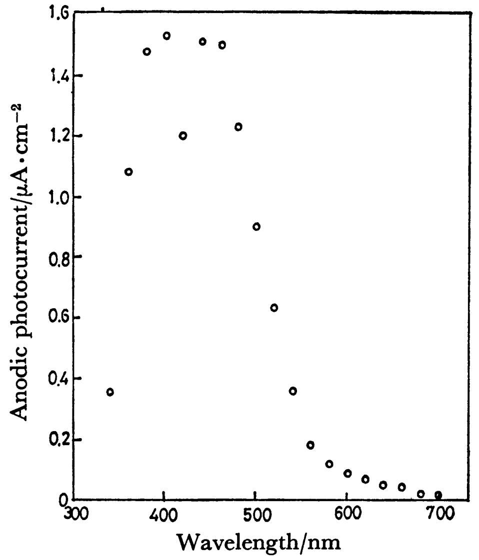

Fig. 3. Action spectrum of anodic photocurrents at $CdSnO_3$ electrode at 0.5 V *vs.* SCE in 1 mol·dm^{-3} NaOH.

the electrode was found to be fairly stable. The anodic polarization to give the total charge of 9.86 C in 0.2 mol·dm^{-3} NaOH caused anodic dissolution of the electrode less than 0.1% of the current efficiency, as determined by atomic absorption analysis of dissolved cadmium. The rest of the charge was believed to be consumed in the evolution of oxygen.

An anodic photocurrent spectrum obtained in 1 mol·dm^{-3} NaOH at 0.5 V *vs.* SCE is shown in Fig. 3, from which the response to light of wavelengths shorter than 700 nm is appreciable. A hollow in the action spectrum, observed in wavelengths between 400 and 440 nm, is believed to be due to the intensity variation in monochromatic light which is characteristics of the xenon lamp. If the assumption is made that the photoresponse is due to band-band transitions, the bandgap of $CdSnO_3$ is then obtained to be 1.77 eV.

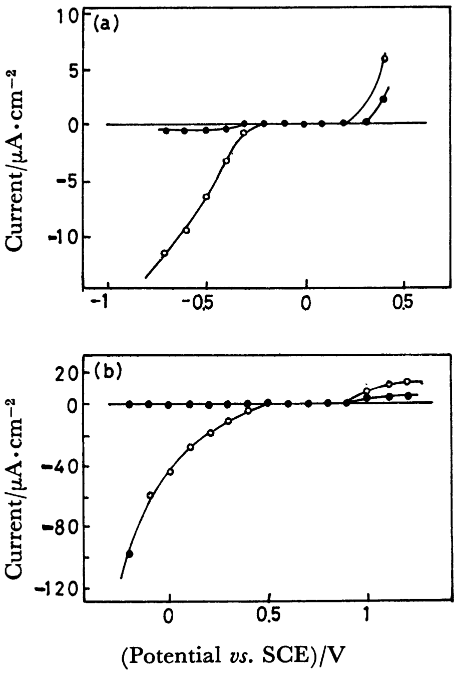

Fig. 4. Steady state current-potential curves of $LaRhO_3$ electrode in (a) 1 mol·dm^{-3} NaOH and (b) 0.5 mol·dm^{-3} H_2SO_4.

●: In the dark, ○: Under illumination.

Photoelectrochemical Properties of $LaRhO_3$ Prepared on the Substrate Pt Plate. Figure 4 shows current-potential curves of the prepared electrode in 1 mol·dm^{-3} NaOH and 0.5 mol·dm^{-3} H_2SO_4. As this figure shows, noticeable photoresponses appear in the cathodic branch. A result obtained for a stability test is given in Fig. 5. As shown in this figure, the photocurrent usually showed a spike at the instant of the on- and off-time of illumination. The appearance of the spike seems to be due to charging currents in capacitive components of the electrode which is not well known at present. It is seen in Fig. 5 that the cathodic photocurrent is so stable as to give almost the constant photocurrent with polarization for as long as 30 min.

Among a variety of oxides, Cu_2O is known to show p-type photoresponse.[10,23] However, this material is quite easily decomposed by both anodic and cathodic polarizations. Compared to this material, $LaRhO_3$ showed no such a serious instability. Judging from the stability of photocurrents shown in Fig. 5, a large part of the cathodic charge consumed during the electrolysis for 30 min must concerned with the evolution of hydrogen. There will be of no doubt, however, that the hydrogen evolution on oxide surfaces must be accompanied with their reduction more or less. A slight decrease in the photocurrent in Fig. 5, observed after the electrolysis for 15 min, may be connected to such an electrode reduction, but still $LaRhO_3$ will be useful as a photocathode at least in aqueous solutions containing another electroactive species besides proton and water if the redox potential of the species is more positive than the hydrogen electrode potential.

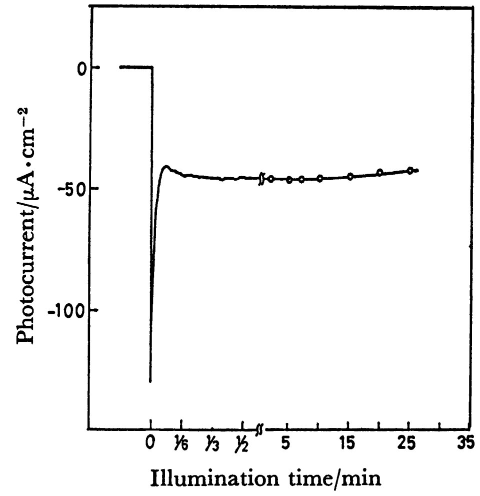

Fig. 5. Stability test of cathodic photocurrent at $LaRhO_3$ electrode at 0 V *vs.* SCE in 0.5 mol·dm^{-3} H_2SO_4.

An action spectrum of the cathodic photocurrent is shown in Fig. 6. Effects of the intensity variation of monochromatic light are again reflected in the action spectrum in the wavelengths between 400 and 440 nm and between 800 and 950 nm. If the threshold wavelength of the electrode, 950 nm, is assumed to be

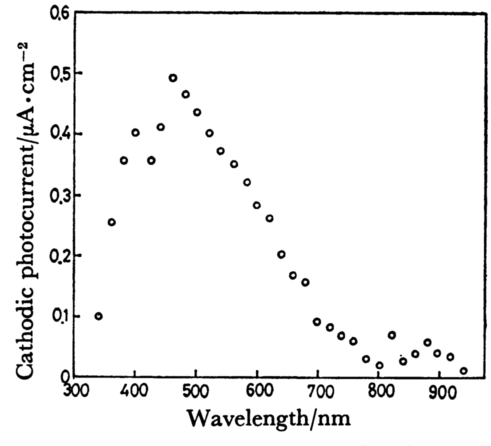

Fig. 6. Action spectrum of cathodic photocurrent at $LaRhO_3$ electrode at 0 V *vs.* SCE in 0.5 mol·dm^{-3} H_2SO_4.

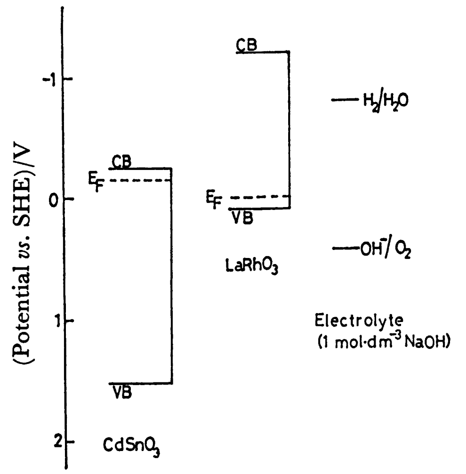

Fig. 7. Energetic correlation between electrodes and 1 mol·dm^{-3} NaOH.

CB, VB, and E_F denote the conduction band, the valence band and the Fermi level of the electrode.

determined by the bandgap of the material, it will then be 1.35 eV.

Energetic Correlation of the Electrode and Electrolytes. Figure 7 shows energetic correlations of $CdSnO_3$ and $LaRhO_3$ electrodes to the hydrogen and oxygen electrodes in 1 mol·dm^{-3} NaOH (pH=13.8). For illustration of this figure, the followings are assumed. (1) The Fermi level of the electrodes locates at 0.1 eV below the conduction band edge for $CdSnO_3$ and above the valence band edge for $LaRhO_3$. (2) The flat-band potential of $LaRhO_3$ electrodes is equal to the onset potential of the cathodic photocurrents.

As shown in this figure, these materials do not efficiently work as photoelectrodes in water photolysis cells, because the efficient photoelectrodes must have both of the energy levels of the hydrogen and oxygen evolution reactions within their bandgaps.(1) In this respect, photoelectrochemical properties of these materials are unsatisfactory. However, these semiconductors may find application fields as photocatalysts in aqueous solutions. An important point lies in that these are superior to other stable semiconductor materials in the point of spectral response to solar energy.

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