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CdS-ELECTROCHEMICAL PHOTOCELL WITH S^{2-} ION-CONTAINING ELECTROLYTE

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S^{2-} ion in the electrolyte of CdS-electrochemical photocell makes the flatband potential of CdS electrode shift remarkably toward the cathodic direction and also makes this electrode photoelectrochemically stable. The possibility of an efficient electrochemical photocell with CdS electrode has been demonstrated by the polarization characteristics.

Since the attractive Honda-Fujishima Effect[1)] on the electrochemical photolysis of water with n-type TiO_2 electrode was discovered,such an electrochemical photocell with a semiconductor electrode has been extensively studied by some investigators. The conversion efficiency of the light energy in such photocells studied by this time , however, is as yet very low. Ohnishi et al.[2)] studied on the quantum yield of the photocell, TiO_2/electrolyte/ Pt, and stated that the very low efficiency as a light convertor of this photocell owed to the small difference between the flatband potential of the TiO_2 electrode and the reduction potential of H^+ ion.

Fujishima et al.[3)] reported that a considerable improvement of the efficiency could be obtained by using an alkaline solution as anolyte for TiO_2 electrode, as the flatband potential of TiO_2 electrode varied linearly with the pH of the solution at the rate of ca. -60mV/pH.

CdS(E_g= 2.4 eV) is preferable to TiO_2(E_g= 3.0 eV) from the viewpoint of the effective utilization of solar energy. But usually CdS is decomposed anodically into Cd^{2+} ion and elementary S in the cell under illumination, and moreover the flatband potential of this electrode does not depend on the pH of the solution.[4)] Therefore, for the effective realization of the electrochemical photocell with CdS electrode, it is necessary to find the way to make CdS electrode photoelectrochemically stable and shift the flatband potential of this electrode toward the cathodic direction. In order to resolve these problems,the effect of the additives, S^{2-} ion etc., in the electrolyte on the polarization characteristics of CdS electrode was investigated in this experiment. Sintered CdS electrodes were here used especially under the practical consideration of realizing a large scale solar cell in the future. In this paper, the important results are described.

CdS disk pellets (13 mm$^{\phi}$, 2 mm thickness) having the density of 2.6 g/ cm^3 were fabricated from pure CdS powder (purity; 99.999%)by the press of 50~60 kg/ cm^2. Then they were sintered at 900~950°C for about one hour in N_2 atmosphere, and cooled slowly down to room temperature. The sintered CdS electrodes obtained have the electric resistance of 1~2× $10^3 \Omega$ cm. Good electrical ohmic contact of sintered CdS with Cu lead wire was ensured by vacuum-evaporated indium. Before the measurement, the surface of the CdS electrode was polished by sand paper, followed by buff-polish with Cr_2O_3 fine powder, chemically polished for 10 sec in concentrated HCl, and then washed throughly with distilled water.

The polarization characteristics of the CdS electrode was measured potentiostatically, using a platinized platinum as counter electrode, saturated calomel electrode as reference electrode and a Xe arc lamp (500 W) for illumination. The differential capacitance of the space charge layer of the CdS electrode was determined by means of the impedance bridge method, in which 5 mV AC voltage was superimposed on the externally applied DC voltage for the polarization.

The Mott-Schottky plots of the differential capacitances of the sintered CdS electrode in the solutions containing various concentrations of S^{2-} ion are shown in Fig. 1. The linearity of these curves shows that the Helmholtz capacitance may be neglected and then the changes of the electrode potential correspond only to the changes of the potential drop across the space charge layer of CdS electrode. Thus the extrapolation crossing point of these curves on the potential axis of these plots corresponds to a potential deviating positively by a value of kT/q from the flatband potential. As shown in Fig. 1, S^{2-} ion alters remarkably the flatband potential of CdS electrode toward the cathodic direction.

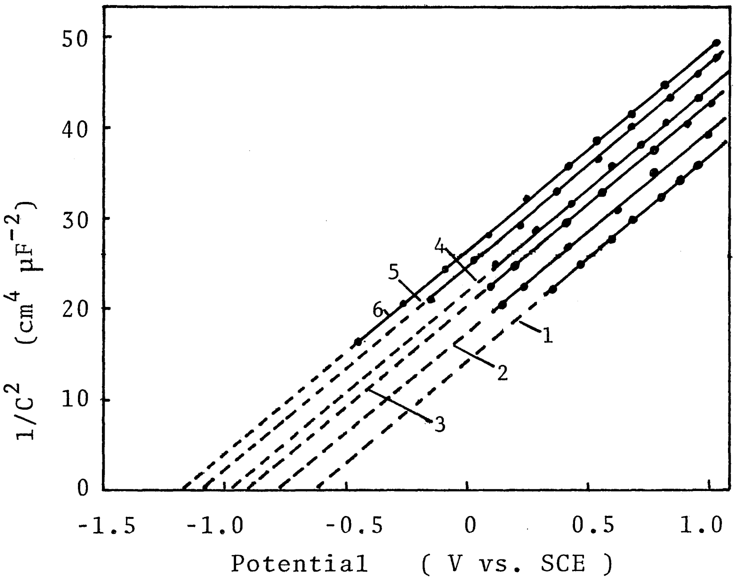


Fig.1 Mott-Schottky plots of the sintered CdS electrode in the solutions containing various concentrations of S^{2-} ion.

1;0 mol/l Na_2S (Basic solution , 1 mol/l Na_2SO_4)
2;10^{-5} mol/l Na_2S 3;10^{-4} mol/l Na_2S
4;10^{-3} mol/l Na_2S 5;10^{-2} mol/l Na_2S
6;10^{-1} mol/l Na_2S

The current-potential curves of the CdS electrode in dark and under illumination in the electrolyte with and without S^{2-} ion are shown in Fig. 2. The anodic dark currents in both solutions are negligibly small($< 10^{-7}$ A/cm^2). The anodic photocurrent in a sintered CdS electrode begins to flow at the same potential of ca. -0.7 V (vs. SCE) in the solution without S^{2-} ion as in the single crystal electrode.

It is shown in Fig. 2 that the S^{2-} ion makes this potential shift to the cathodic side by ca. 0.7 V. This fact is qualitatively in good agreement with the fact in the capacitance data (Fig.1) . This phenomenon is very favourable for improving the characteristics of the electrochemical photocell and developing more efficient electrochemical photocell.

Possible anodic reactions on CdS electrode under illumination in the solution with S^{2-} ion are as follows;

(1) Dissolution of CdS

$$CdS + 2p \rightarrow Cd^{2+}_{aq} + S$$

p: positive hole

$$Cd^{2+}_{aq} + S^{2-}_{aq} \rightarrow CdS$$

(2) Oxidation of S^{2-} ion

$$S^{2-}_{aq} + 2p \rightarrow S$$

If reaction (1) occurs, Faraday's law must be hold between the amount of electricity and the amount of dissolved Cd^{2+} ion (CdS precipitates) . On the other hand, if reaction (2) takes place, Cd^{2+} ion or CdS precipitates will not exist in the electrolyte. To determine whether the anodic photocurrent is attributed to reaction (1) or (2) , the amount of dissolved Cd^{2+} ion was quantitatively determined by atomic absorption spectrophotometry. The amount of dissolved Cd^{2+} ion at the experiment in the solution without S^{2-} ion agrees well with the value calculated from the amount of the flowed electricity, while dissolved Cd^{2+} ion was scarcely detected in the solution containing the appropriate amount of S^{2-} ion.

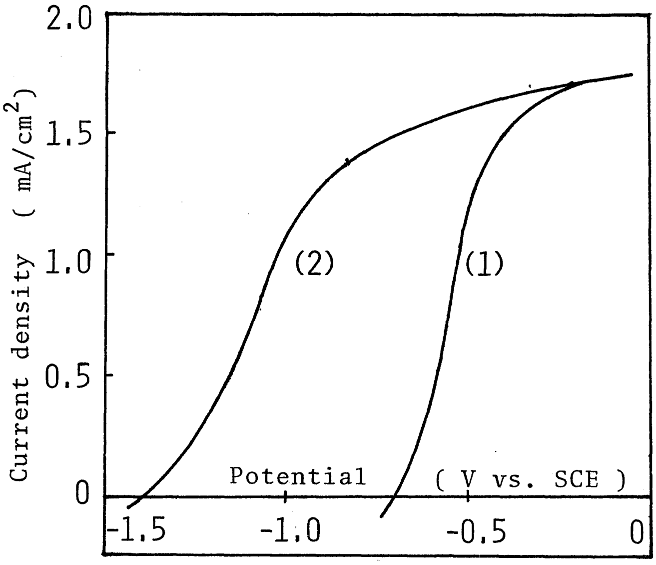


Fig.2 Current-potential curves for the sintered CdS electrode in the solution without S^{2-} ion (1) and with S^{2-} ion of 10^{-2} mol/l (2).

From these facts, it can be concluded that S^{2-} ion in the electrolyte makes the flatband potential of CdS electrode shift toward the cathodic direction and this electrode photoelectrochemically stable.

When the electrode surface will be gradually covered with elementary S by reaction (2) , the photocurrent will decrease correlatively. To prevent the deterioration, SO_3^{2-} ion was added into the solution. Fig.3 shows the typical current-time curves in the solution with and without SO_3^{2-} ion. The photoelectrochemical reaction was performed at -1.05 V (vs. SCE) in both cases. This result shows that SO_3^{2-} ion suppresses the decrease by S of the photocurrent. This may be due to the dissolution of the deposited elementary S into SO_3^{2-} ion, resulting in the formation of $S_2O_3^{2-}$ ion.

In the electrochemical photocell, one being one-electrolyte system cell and the other being two-electrolyte system cell, sintered CdS electrode as anode and Pt electrode as cathode were set in the above mentioned electrolyte. In the latter cell, the anode in anolyte(the above mentioned electrolyte) was separated by a salt bridge(resistance,0.5kΩ) from catholyte having lower pH than anolyte. The relation

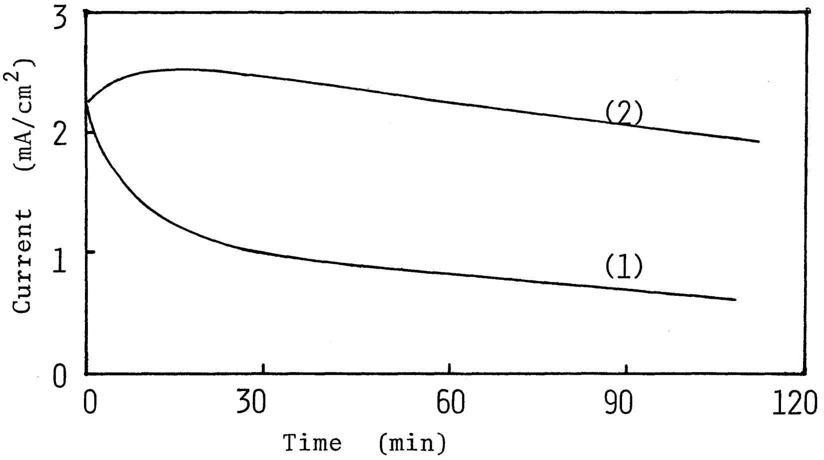
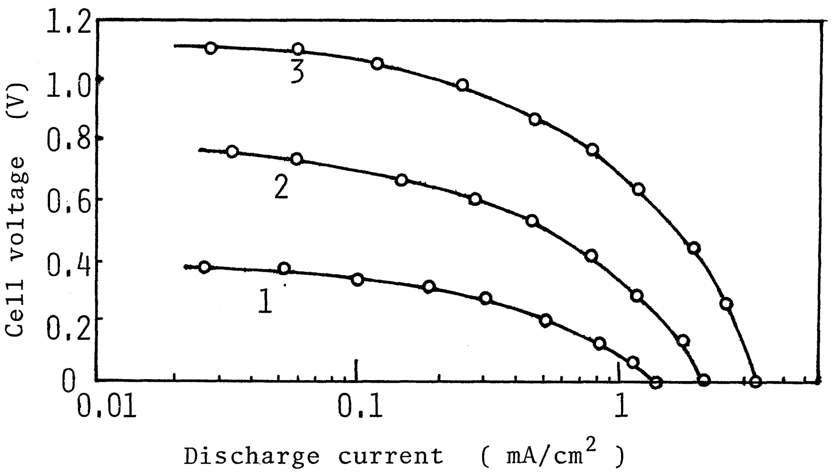


Fig.3 Current-time curves for the sintered CdS electrode polarized at -1.05 V (vs.SCE) in the solution (1);1 mol/l Na_2SO_4+0.05 mol/l Na_2S solution and (2);1 mol/l Na_2SO_3+ 0.05 mol/l Na_2S solution.

Fig.4 Cell performances.
1;One-electrolyte system cell
Electrolyte;2 mol/l Na_2SO_3+ 0.2 mol/l Na_2S solution
2,3;Two-electrolyte system cell
Anolyte
2 mol/l Na_2SO_3+0.2 mol/l Na_2S solution
Catholyte
2;1 mol/l Na_2SO_4 solution (pH 7)
3;1 mol/l Na_2SO_4 solution (pH 1)
Light source; Xe lamp



between discharge current and cell voltage on the cell performance is shown in Fig. 4. The output power of these cells under the sunlight on a fine summer day was comparable to that in Fig.4 under Xe lamp. The current efficiency of the hydrogen generation at the cathode reached 100% in some optimum condition.

References

1) A.Fujishima and K.Honda, Nature, 238, 37 (1972).
2) T.Ohnishi, Y.Nakato, and H.Tsubomura, Ber. Bunsenges. physik. Chem., 79, 523 (1975).
3) A.Fujishima, K.kohayakawa, and K.Honda, Bull. Chem. Soc. Japan, 48, 1041 (1975).
4) T.Watanabe, A.Fujishima, and K.Honda, Chem. Lett., 897 (1974).

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