In Situ Optical Absorption Spectra during Photoassisted Electrochemical Intercalation/Deintercalation of Hydrated K^+ Ions into/from Single Crystal $2H-SnS_2$

Takashi SHIBATA*, Takashi MIURA, Tomiya KISHI and Takashi NAGAI

Received July 31, 1989; Accepted October 14, 1989

Abstract

In situ optical absorption and X-ray diffraction measurements of a single crystal $2H-SnS_2$ electrode during cathodic and anodic polarization in 1M KCl with and without irradiation indicated that both the intercalation and deintercalation of hydrated K^+ ion were photoassisted, and that the intercalation over some limit was topotactically irreversible.

1 Introduction

As described in review papers¹⁻⁴⁾, many researches have been published on the photoassisted intercalation/deintercalation of ions into/from various electrode materials as related to the conversion and storage of solar energy, electrochromic devices, ion pumps, sensors and also to the basic analyses of photosynthesis and biological neurotransmitter.

We first reported previously⁵⁻⁶⁾ the photoelectrochemical behavior of SnS_2 and $SnSe_2$ (IV-VI compounds) in a 1M KCl aqueous solution ($M = \text{mol/dm}^3$). Since the intercalated compound, $K_xSnS_2(H_2O)_y$, is oxidized easily by air, it is preferable to investigate the actual state of electrochemical phenomena by various in situ measurements. Thus, in situ absorption spectrum and X-ray diffraction measurements have been attempted for a single crystal $2H-SnS_2$ electrode in this study.

2 Experimental

The electrochemical cell for the in situ observation was shown in Fig. 1. The electrode holder "b" was not immersed in the electrolyte but mounted in a cell wall "a". Single crystal $2H-SnS_2$ was cut to a disk (6.3 mm in diameter) by a specially designed cutter without giving any damage and its circular contacting area with an electrolyte had a diameter of 4.5 mm. This thin and mechanically weak SnS_2

disk was supported by a quartz disk on which gold was electroless plated to form an ohmic contact excepting the paths for a light beam. The cell with a quartz window was made of Teflon. All measurements were carried out in a 1M KCl aqueous solution under nitrogen atmosphere, using a Pt counter electrode and an Ag/AgCl(TOA, HS-305DS) reference electrode. By a double beam spectrophotometer (JASCO, UVIDEQ-1), in situ absorption spectra of SnS_2 were obtained with reference to a blank cell without an SnS_2 crystal, where the incident beam was set perpendicular to the c-plane of SnS_2 .

Fig. 1 Illustrated electrochemical cell for in situ optical absorption measurements.

"a": Chamber part, "b": Electrode holder. 1; Quartz disk 2; Silicon O-ring 3; Electrolyte 4; Pt counter electrode 5; Gas inlet 6; Ag/AgCl reference electrode 7; Sample crystal 8; Au plated quartz disk 9; lead to working electrode.

Department of Applied Chemistry, Faculty of Science and Technology, Keio University (Hiyoshi 3-14-1, Kouhoku-ku, Yokohama, 223 JAPAN)

Key Words: single crystal SnS_2 , in situ optical absorption spectra, photoassisted intercalation

The amount of electricity was monitored by a coulombmeter (Hokuto Denko, HF-102) connected with a potentiostat (Toho Technical Research, Model-2020). A 500W Xe lamp (Ushio, Lamp house: UI-501 S/NB K058, Lamp: UXL-500D-O, Light source: UI-501C) was used for a light source, and the cell should be removed from the spectrometer during the experiments under illumination.

3 Results and Discussion

Figure 2(A) compares cyclic voltammograms of an SnS_2 electrode in dark and under illumination. The cathodic current bending down at -850 mV is increased by illumination, which is evidenced more clearly by potentiostatic experiments as seen in Fig. 2(B). It is worth to note that SnS_2 , an n-type semiconductor, shows cathodic photoresponse to irradiation. Although the reductive decomposition of SnS_2 to form SnS_{2-x} is a main reaction in dark, the intercalation of K^+ ions proceeds competitively under illumination⁵⁻⁶. The reverse anodic current is also increased by illumination corresponding to the photoassisted deintercalation of inserted K^+ ions.

Fig. 2(A) Cyclic voltammograms (1st cycle of) under illumination (solid) and in dark (dashed).

a: cathodic turning potential at -815 mV, dark and photocurrents are overlapped. b: cathodic turning potential at -850 mV. sweep rate; 50 mV/s.

(B) Effect of chopped illumination on potentiostatic (-850 mV) cathodic current.

When K^+ ions are inserted to SnS_2 , the surface appearance changes to blue from its original color of yellowish orange. This cation insertion reaction,

however, proceeds not homogeneously but inhomogeneously as seen in Fig. 3(A). The EPMA results of potassium in Fig. 3(B) indicate clearly the localized K^+ ion insertion.

Fig. 3 (A) SEM, and EPMA photographs for (B) $\text{K}(\text{K}\alpha)$, (C) $\text{S}(\text{K}\alpha)$ and (D) $\text{Sn}(\text{L}\alpha)$ after cathodic polarization in dark.

-349 mV (rest potential) ~ -900 mV; 0.5 mV/s.

Fig. 4 In situ X-ray diffraction patterns of the intercalated compound.

In this paper, the apparent K content in SnS_2 , x , was calculated from the initial weight of a crystal and the net amount of cathodic charge externally flowed: $x=e/\text{Sn}$. In situ X-ray diffraction data showed that the intercalated compound ($x=0.3$) formed at -900 mV in dark has a interlayer gap, d , of $8.90(2)$ Å and that its diffraction intensity increases with x as in Fig. 4. When the cathodic polarization is carried out at -900 mV under illumination, on the other hand, the d value of $8.83(1)$ Å is observed at $x=0.3$.

Original 2H-SnS_2 has $5.899(1)$ Å of d . The K-insertion compounds of $\text{K}_x\text{SnS}_2(\text{H}_2\text{O})_y$ ⁷⁾ and KSnS_2 ⁸⁾ are reported to have d values of 9.30 and 8.536 Å, respectively. The above results suggest that the intercalation product in dark is distinct from that under illumination. A preliminary TGA-DTA result revealed that about one and two molecules of water is co-intercalated with one K^+ ion in dark and under illumination, respectively.

A typical absorption spectrum of SnS_2 crystal itself is shown in Fig. 5. The oscillation arises from the interferential reflection from the front and back faces of a thin crystal. After connecting midpoints of a oscillating curve, a real spectrum is shown in Fig. 6 (curve 0). Single crystal SnS_2 has an absorption edge of 571 nm in case of $\langle 001 \rangle$ incident beam.

Fig. 5 Optical absorption spectrum of single crystal 2H-SnS_2 .

No change in the spectra is caused by the polarization at above -815 mV, where no cathodic reaction takes place virtually. Fig. 6(A) and 6(B) show the absorption spectra after polarized more negatively (-850 mV) in dark and under illumination, respectively. A sample polarized under illumination shows high absorbance at 550 nm compared with that polarized in dark, which suggests that the insertion of hydrated K^+ ion is accelerated and the reductive decomposition of SnS_2 is suppressed by illumination. The broad absorption at >550 nm, corresponding to the formation of allowed electronic states in the band gap, becomes the sharper after the more progressive intercalation as seen in Fig. 6. This absorption is due presumably to the charge transfer from the intercalant to the layered host lattice, and is not caused by decomposition of the lattice itself. Although McCanny calculated the electronic structure of an intercalation compound LiSnS_2 by the semi-empirical method⁹⁾, there is little information about that of analogous intercalation compounds with a hydrated cation.

Another experimental result indicated that the intercalation can proceed even at -815 mV after the initiation of a cathodic reaction at -850 mV, which suggests that the lattice defects introduced by the preceding polarization may accelerate the cation insertion reaction.

Two curves of A in Figs. 6(A) and 6(B) show the absorptin spectra of a reoxidized sample, where the broad absorption at around 700 nm disappears by the anodic deintercalation reactin, though the spectrum does not recover its initial shape perfectly. Although Schöllhorn et al.⁷⁾ reported that the chemical intercalation of hydrated alkali metal ions into SnS_2 powder proceeds topotactically, the electrochemical insertion reaction of K^+ ion does not exhibit a perfect topotactic reversibility along the c -axis of SnS_2 .

As seen on anodic branches in Fig. 2 and as recognized in another potentiostatic experiment under chopped irradiation, the anodic current after cathodic processes is increased by illumination. The main anodic reaction is the deintercalation of inserted K^+ ions as evidenced by in situ measurements (see Figs. 6(A) and 6(B)). Accordingly, the electrochemical insertion/extraction of hydrated K^+ ions into/from SnS_2 is photoassisted bi-directionally, though whose excitation mechanism is not understood at present.

Fig. 6 In situ absorbance of polarized crystal (A) in dark and (B) under illumination.

0; Original SnS_2 , C1-C4; cathodized, A; anodized from C4, $x=0.0025$ (C1), 0.0050(C2,A), 0.0075(C3), 0.0100(C4).

As mentioned above, the optical interference of a thin lamellar crystal is observed even when it is in contact with a solution. The optical thickness of such a crystal can be determined from the oscillating frequency also after intercalation, though unsuccessful in the present case because of the lack of perfect flatness of the sample. In situ determination of a lattice parameter along the beam direction may also be possible in general within the accuracy of $\pm 10^{-3} \text{ \AA}$.

4 Conclusions

Changes in electronic and crystallographic structures of SnS_2 induced by the electrochemical reactions have been revealed by in situ measurements. In order to discuss the precise absorption spectrum of an intercalated compound, some improvements of an experimental set-up is required. Succeeding papers will describe the electrochemical phenomena in more detail.

We wish to thank Mr. Nobuo Ebina of Ebina Denka Kogyo Co., Ltd. for the instruction of electroless gold plating on quartz; Dr. Eiji Ohta for helpful discussions; Mr. Kesao Aihara for the processing of the cell.

References

- 1) H. Tributsch, *Solid State Ionics*, **9-10**, 41 (1983).
- 2) Y. Takeda, *Nihonkagakutogyutu*, **91** (1986).
- 3) H. Nakamatsu, T. Kawai and S. Kawai, *Kagakukougyou*, **3**, 219 (1984).
- 4) T. Asai and S. Kawai, *Hyoumen*, **23**, 189 (1985).
- 5) T. Shibata, T. Miura, T. Kishi and T. Nagai, *Proceeding of 53rd Annual Meeting Electrochem. Soc. Jpn.*, **F201** (1986).
- 6) T. Shibata, Y. Muranushi, T. Miura and T. Kishi, *Proc. '88 Fall Meeting Electrochem. Soc. Jpn.*, **D220** (1988).
- 7) R. Schöllhorn, W. Roer and K. Wagner, *Monatsh. Chem.*, **110**, 1147 (1972).
- 8) A. Leblanc, M. Danot and J. Rouxel, *Bull. Soc. Chim. Fr.*, **1**, 87 (1969).
- 9) J.V. McCanny, *Phys. Stat. Sol.(b)*, **93**, K29 (1979).