Photo-rechargeable Battery Based on Photo-induced Copper Intercalation into Quasi-One-Dimensional Compound KFeS$_2$

Shogo Takenoshita, Rui Yatabe, Masatoshi Kozaki, Hisao Kuriyaki and Kiyoshi Toko

Department of Electronics, Graduate School of Information Science and Electrical Engineering, Kyushu University
744, Motooka, Nishi-ku, Fukuoka 819-0395, Japan
Phone: +81-92-608-3729 E-mail: s.takenoshita@nbelab.ed.kyushu-u.ac.jp

1. Introduction
Lithium-ion battery, which is used for portable electronic devices such as cellular phone, is charged and discharged using intercalation reaction. Intercalation is the insertion of ions or molecules into interlayer of layered materials or interchain of one-dimensional materials [1].

Photo-rechargeable battery is a device that can convert photo-energy to electrical energy and store it. Photo-rechargeable battery is firstly reported by Tributsch [2]. He proposed that it could be charged by photo-induced intercalation of ions into p-type layered semiconductor such as ZnSe or ZrSe$_2$. Zou et al. reported photo-rechargeable battery using composite electrode made by carbon fiber and TiO$_2$ [3]. Saito et al. prepared the photo-rechargeable cell using three electrodes; energy conversion electrode, charging electrode and counter electrode [4, 5]. Until now some photo-rechargeable batteries have been proposed [6, 7], however, no remarkable results have yet been reported.

We are developing a novel photo-rechargeable battery using quasi-one-dimensional compounds KFeS$_2$. The crystal structure of KFeS$_2$ is shown in Fig. 1. It has a quasi-one dimensional structure (monoclinic; $a = 0.7084$ nm, $b = 1.1303$ nm, $c = 0.5394$ nm and $\beta = 113.2^\circ$) consisting of FeS$_4$ tetrahedra linked at their edges along c-axis [8]. In this paper, we report the effect of irradiation to photo-rechargeable battery fabricated using KFeS$_2$ electrode.

2. Experimental
K$_2$CO$_3$ (99.5%), Fe (99.99%), S (99.999%) and Na$_2$CO$_3$ (99.5%) as flux, were placed into a quartz tube with an internal diameter of 16mm and heat treated at 920$^\circ$C for 4h in argon atmosphere. The resulting compound was cleaned in water for 10h to remove the flux and unwanted by-products. Then, the resulting crystals were annealed at 300$^\circ$C in a vacuum for 2days. They were black needle-shaped crystals oriented along the c-axis direction. For the high conductivity, the crystals were heat treated at 100$^\circ$C for 2days in iodine atmosphere [9].

Powdered KFeS$_2$ crystals were appropriately mixed with polyvinyl chloride as a binder. The mixture was pressed into a pellet of $10$ mm$\Phi \times 0.5$ mm at 3tons/cm$^2$. The electrode with the surface area of about 0.2 cm$^2$ was cut out from the pellet. The electrical contact was made with gold paste. The experimental setup is shown in Fig. 2. The working electrode (WE) and Pt counter electrode (CE) was set in the cell made of quartz. The electrolyte was 0.05mol/L CuSO$_4$ and 0.01g I$_2$. The WE was irradiated by a Xe lamp of 20 mW/cm$^2$.

3. Result and Discussion
For photo-intercalation into KFeS$_2$ the WE was irradiate for 20 minutes without connecting of WE and CE, and the discharge current which flowed through a resistance of 5k$\Omega$ connecting of WE and CE was measured in the dark (Fig. 3). The discharge current over 10 $\mu$A/cm$^2$ was observed for about 50 minutes. The photo-charged quantity ($Q_{ph}$) calculated from the time integration of discharge cur-
rent from the irradiation start to 80 minutes was about 56 mC/cm². The irradiation time dependence of the $Q_{ph}$ is shown in Fig. 4. It was found that the $Q_{ph}$ was increased in proportion to irradiation time almost.

The WE was irradiated intermittently by a Xe lamp at an interval of 10 minutes, and the electromotive force (EMF), which is the open-circuit voltage of WE and CE, was measured. The time dependence of the EMF under dark and irradiation alternately is shown in Fig. 5. The EMF was increased with the irradiation time, but maintained almost the constant value under irradiation stop. From the results, it was confirmed that the cell was charged by photo-induced copper intercalation into KFeS₂.

### 4. Conclusions

We have developed a novel photo-rechargeable battery using quasi-one-dimensional compound KFeS₂.

As results, i) the photo-charged quantity was increased in proportion to irradiation time, ii) the EMF was increased with the photo-irradiation time, but maintained almost the constant value under irradiation stop. From the results, it was confirmed that the cell was charged by photo-induced copper intercalation into KFeS₂.

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### References