Extended Abstracts of the 2011 International Conference on Solid State Devices and Materials, Nagoya, 2011, pp326-327

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 ZeS_2 or $ZrSe_2$. Zou *et al.* the 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 β = 113.2°) 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.

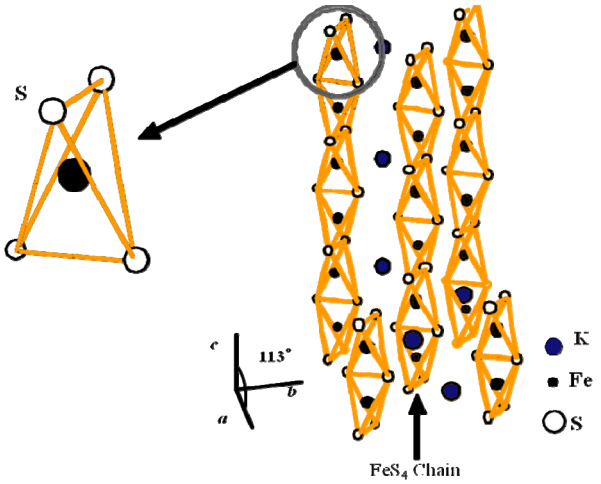

Fig. 1 Crystal structure of $KFeS_2$

2. Experimental

K_2CO_3 (99.5%), Fe (99.99%), S (99.999%) and Na_2CO_3 (99.5%) as flux, were placed into a quartz tube with an internal diameter of 16mm and heat treated at 920℃ 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℃ 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℃ 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 mmΦ × 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.

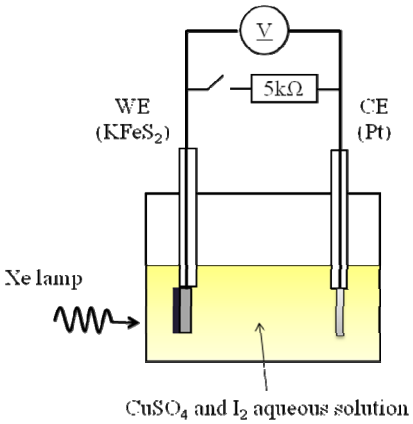

Fig. 2 Experimental setup

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 5kΩ connecting of WE and CE was measured in the dark (Fig. 3). The discharge current over 10 μA/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/cm^2. 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.

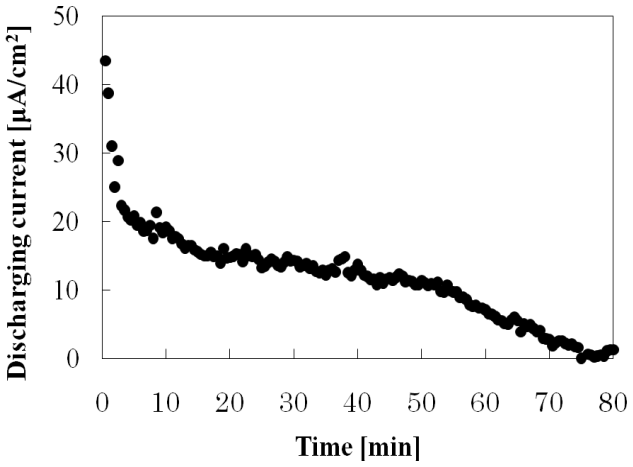

Fig. 3 Discharging current after photo-irradiation for 20 minutes

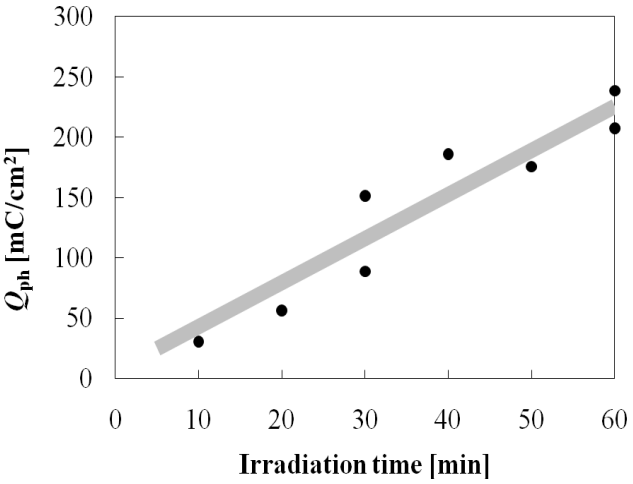

Fig. 4 Irradiation time dependence of the Q_{ph}

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, which indicated that the self-discharge was small. The EMF was about 0.21V in irradiation time of 30 minutes. The increase of EMF is considered to derive from photo-induced intercalation of copper ions into FeS_4 chains of $KFeS_2$.

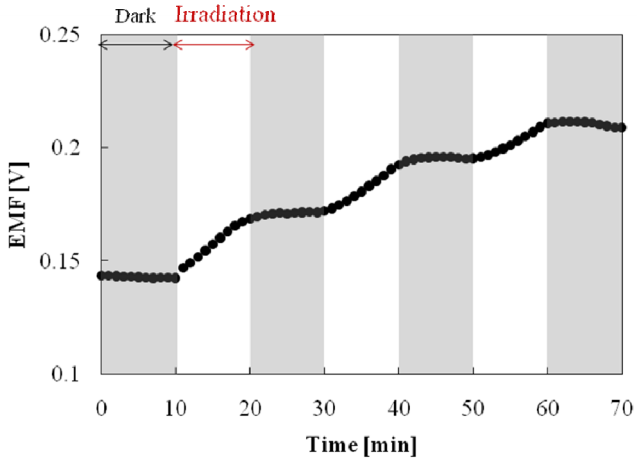

Fig. 5 Time dependence of the EMF under dark and irradiation alternately

4. Conclusions

We have developed a novel photo-rechargeable battery using quasi-one-dimensional compound $KFeS_2$.

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 $KFeS_2$.

Acknowledgement

This study was supported by Grants-in-Aid for Scientific Research (No. 23656062) from the Ministry of Education, Culture, Sports Science and Technology, Japan.

References

[1] M. S. Whittingham and A. J. Jacobson: *Intercalation Chemistry* (Academic Press, New York, 1982) p.27.

[2] H. Tributsch: Appl. Phys. **23** (1980) 61.

[3] X. Zou, T. Nagao, O. Miyamoto, T. Nomiyama, Y. Horie and T. Miyazaki: Jpn. J. Appl. Phys. **43** (2004) 7707.

[4] Y. Saito, S. Uchida, T. Kubo and H. Segawa: Thin Solid Films.**518** (2010) 3033.

[5] Y. Saito, A. Ogawa, S. Uchida, T. Kubo and H. Segawa: Chem. Lett. **39** (2010) 488.

[6] A. K. Pandey, P. C. Deakin, R. D. Jansen-Van Vuuren, P. L. Burn and I. D. W. Samuel: Adv. Mater. **22** (2010) 3954.

[7] T. Miyasaka, N. Ikeda, T. Murakami and K. Teshima: Chemistry Letters **36** (2007) 480.

[8] W. Bronger, A. Kyas and P. Muller: J. Solid State Chem. **70** (1987) 262.

[9] H. Kuriyaki, K. Takenaka: Jpn. J. Appl. Phys. **43** (2004) 188.