## ZnSe:CIGS 粉末光カソードの粒径制御による性能向上と電気化学的手法を用いた表面・バルク特性評価

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Improvement of Photoelectrochemical Performances of Particulate ZnSe:CIGS Photocathodes by Particle Size Control and Electrochemical Evaluation for Surface and Bulk Characteristics (<sup>1</sup>Graduate School of Engineering, Shinshu University, <sup>2</sup>Reseach Initiative for Supra-Materials, <sup>3</sup>The University of Tokyo)  $\bigcirc$  Fumiaki Takagi<sup>1</sup>, Yosuke Kageshima<sup>1,2</sup>, Katsuya Teshima<sup>1,2</sup>, Kazunari Domen<sup>2,3</sup>, Hiromasa Nishikiori<sup>1,2</sup>

Particulate ZnSe:CIGS (a solid solution of ZnSe and CuIn<sub>0.7</sub>Ga<sub>0.3</sub>Se<sub>2</sub>) photocathodes have the absorption edge at 800 – 900 nm and are active for photoelectrochemical (PEC) reduction of water under simulated sunlight<sup>1</sup>). Since the as-synthesized ZnSe:CIGS powder possess wide size distribution ranging from submicron to several tens of micron, inadequate size of particles with low photocatalytic activities should possibly coexist. Therefore, there are still room for improvement of PEC performances of the particulate photocathodes *via* the particle size control.

In this study, we classified the as-synthesized ZnSe:CIGS powder into three categories of particle sizes with average sizes of 14.2  $\mu$ m (Large), 4.46  $\mu$ m (Middle) and 1.09  $\mu$ m (Small), and evaluated the PEC performances of the classified ZnSe:CIGS photocathodes. The photocathode made from "Middle" exhibited lager photocurrent than unclassified one in all potential range (Fig.1). The origin of the particle size dependence of the PEC performances were evaluated by various electrochemical measurements in detail. We revealed that the PEC performances of particulate photocathodes were determined by the trade-off between "the number of active sites (Pt)", "the carrier density" and "the resistance of the bulk particles"<sup>2)</sup>.

Keywords: Hydrogen evolution; Photocathode; Photocatalyst, Photoelectrochemistry

ZnSe:CIGS(ZnSe と CuIn<sub>0.7</sub>Ga<sub>0.3</sub>Se<sub>2</sub>の固溶体)粉末光カソードは、800-900 nm 付近に 吸収端を有し、疑似太陽光照射下で水の光電気化学的還元反応に活性な材料である  $^{1}$ 。 合成直後の ZnSe:CIGS 粉末はサブミクロン〜数十ミクロンの広い粒度分布を有する ため、光触媒活性の低い不適切な粒径の粉末が混在している可能性がある。そのため、

粒径制御による粉末光カソードの活性改善の余地があると 考えられる。

本研究では、合成した ZnSe:CIGS 粉末を、平均粒径が 14.2  $\mu$ m (Large)、4.46  $\mu$ m (Middle)、1.09  $\mu$ m (Small)の粉末に分級し、各粒径から成る粉末光カソードの光電気化学(PEC)特性を評価した。粒径が Middle の粉末から成る光カソードが、すべての電位領域で分級前より活性が向上した(Fig.1)。粉末光カソードの PEC 特性の粒径依存性について、ストリッピングボルタンメトリーや電気化学インピーダンス測定等の各種電気化学測定を用いて詳細な解析を実施した。「粉末光カソードの活性点(Pt)の数」・「キャリア密度」・「バルクの抵抗値」のトレードオフが、粉末光カソードの PEC 特性に影響していることを明らかにした $^{2}$ )。

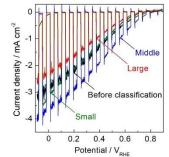


Fig.1 Current-potential curves for the photocathodes composed of different particle size of ZnSe:CIGS.

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- 2) F. Takagi, et. al., Sustainable Energy Fuels, in press, DOI:10.1039/D0SE00998A.