

Direct Photoconversion of Toluene to Methylcyclohexane Using ZnSe:Cu(In,Ga)Se₂ Photocathode

Yosuke Kageshima¹, Yosuke Goto¹, Sho Sugisaki¹, Hiroyuki Kaneko¹, Tsutomu Minegishi^{1,2}, Kazunari Domen¹

¹Department of Chemical System Engineering, Graduate School of Engineering, The University of Tokyo, Tokyo, Japan

²JST PRESTO, Tokyo, Japan

*E-mail: domen@chemsys.t.u-tokyo.ac.jp

Methylcyclohexane (MCH) is well known as one of the most promising candidates of hydrogen carrier, due to its relatively high hydrogen storage density per unit volume (47.4 kg-H₂/m³-MCH), existence in liquid phase at wide range of temperature (-95 to 101°C), and easy discharge of hydrogen [1]. Photoelectrochemical (PEC) hydrogenation of toluene (TL) combined with oxidation of water has also been reported to produce MCH, which can represent not only application of MCH as a hydrogen carrier but also one possible means of the reaction system as an artificial photosynthesis [2-4]. However, sunlight-driven MCH production has not been achieved so far. In the present study, a novel membrane-electrode assembly (MEA) was fabricated from a photocathode consisting of solid solution of ZnSe and Cu(In,Ga)Se₂ (ZnSe:CIGS) [5,6] in order to apply for solar MCH production from TL and water.

The ZnSe:CIGS powder was synthesized by solid state reaction and fabricated into photocathode by the particle transfer method [7]. The obtained particulate ZnSe:CIGS photocathode was modified with CdS, surface conductor layer, and Pt active sites successively [8], and hot-pressed with an anion-exchange type membrane. The PEC reaction was performed in a two-chamber cell, where neutral aqueous electrolyte, 1 M potassium phosphate buffer solution, and TL were separated by the ZnSe:CIGS-based MEA such that the surface of the photocathode was facing to TL side. Simulated sunlight adjusted to AM1.5G was used as a light source.

The ZnSe:CIGS-based MEA successfully generated -0.22 mA cm⁻² of photocurrent at

+0.16 V_{RHE} 1 min after the onset of the PEC reaction as shown in Figure 1. Although the photocurrent gradually decreased over time, it was observed to be recovered after an interval of dark condition, indicating that diffusion process of reactants should limit the reaction. The overall faradaic efficiency (FE) of MCH production reached to 69% after 3 h of PEC reaction, where remaining FE was considered to be consumed by the competitive hydrogen evolution or oxygen reduction reaction. In the presentation, we will discuss about the effects of MEA structure and surface modification for photocathode on FE of the reaction in detail.

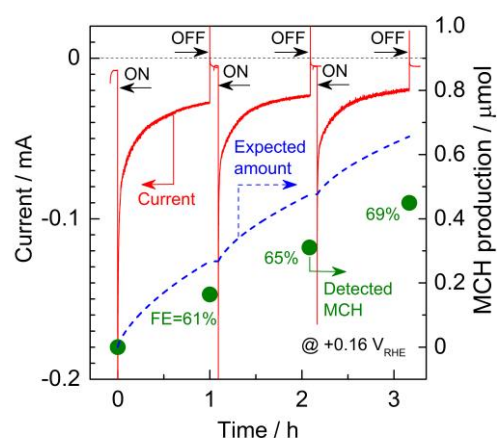


Fig. 1 Time courses for the photocurrent, expected amount of evolved MCH, and actual yield of MCH detected by GC/FID during the PEC MCH production using Pt/Mo/Ti/CdS layer modified ZnSe:CIGS MEA under illumination of simulated sunlight. Geometric surface area of the photocathode was 0.45 cm². 1 M potassium phosphate buffer solution (pH 7) was used as an aqueous electrolyte.

REFERENCES

- [1] R. B. Biniwale, et. al., *Int. J. Hydrogen Energy*, 33 (2008) 360.
- [2] P. Wang, et. al., *J. Am. Chem. Soc.*, 134 (2012) 2469.
- [3] V. Kalousek, et. al., *ChemSusChem*, 7 (2014) 2690.
- [4] Y. Kageshima, et. al., *ChemSusChem*, (2016) in press, doi: 10.1002/cssc.201601758.
- [5] H. Kaneko, et. al., *Adv. Funct. Mater.*, 26 (2016) 4570.
- [6] Y. Goto, et. al., The 118th annual meeting of CATSJS (2016) P010.
- [7] T. Minegishi, et. al., *Chem. Sci.*, 4 (2013) 1120.
- [8] H. Kumagai, et. al., *J. Mater. Chem. A*, 3 (2015) 8300.