Electrosynthesis of glycine from oxalic acid using titanium dioxide electrocatalyst

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Keywords: Amino Acid; Titanium Dioxide; Electrosynthesis; Biomass

The reductive amination of α-keto acids is expected to be a futural synthetic process for amino acid production due to its simplicity and favorable product selectivity. Electrochemically driven amination of α-keto acids, which utilizes water and renewable electricity as hydrogen and energy sources, can realize environment-friendly synthesis of amino acids. Recently, we have reported that TiO_2 grown on Ti mesh electrode (TiO_2/Ti mesh) catalyzes the electrochemical conversion of α-keto acids into the corresponding amino acids in the presence of NH_2OH with remarkably high Faradaic efficiency, i.e, 77–99%.[1)] In this study, we focus on oxalic acid, which is easily produced from agro-waste, as a starting material to generate a precursor of glycine, i.e., glyoxylic acid.[2)] The electrochemical reaction starting from oxalic would realize one-step electrochemical synthesis of glycine (Fig. 1).

Electrochemical measurements such as cyclic voltammetry (CV) and chronoamperometry (CA) for the solution of oxalic acid and/or NH_2OH were performed using a single and a two-compartment electrochemical cell, respectively, equipped with Ag/AgCl electrode and Pt coil as reference and counter electrodes. We applied metal foils, calcined metal foils (450 ºC, 1 h.), and TiO_2/Ti mesh as a working electrode. TiO_2/Ti mesh was prepared from Ti mesh through two-steps hydrothermal reaction as reported in ref. 3). TiO_2/Ti mesh with thin TiO_2 layer (thin-TiO_2/Ti mesh) was prepared by adjusting the reaction time. After CA experiments, catholyte was analyzed by ^{1}H NMR to estimate Faradaic efficiencies (FEs) for production of glycine, glyoxylic acid oxime, and glycolic acid.

CV measurements revealed that calcined Ti foil exhibits higher catalytic activity for oxalic acid reduction than that for NH_2OH reduction (Fig. 2a). Therefore, we performed CA experiments using calcined Ti foil as working electrode. As a result, glycine and its intermediate, i.e., glyoxylic acid oxime were obtained with FEs of 28 and 28%, respectively (Fig. 2b).[4)] Then, we newly prepared TiO_2/Ti mesh having thin TiO_2 layer on Ti surface similarly to calcined Ti foil (thin-TiO_2/Ti mesh) and applied it to the glycine synthesis. After the optimization of reaction conditions, we achieved high FEs of 59 and 14% for glycine and glyoxylic acid synthesis from oxalic acid.

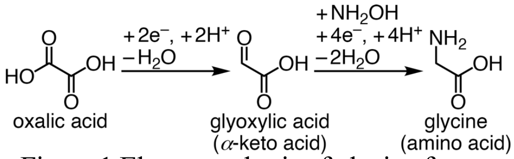

Figure 1 Electrosynthesis of glycine from oxalic acid

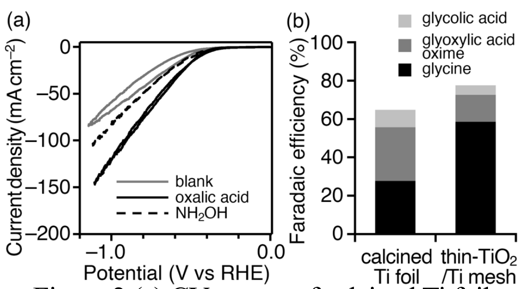

Figure 2 (a) CV curves of calcined Ti foil and (b) products of the CA experiments

1) T. Fukushima, M. Yamauchi, *Chem. Commun.* **2019**, *55*, 14721. 2) R. Watanabe, M. Yamauchi, M. Sadakiyo, R. Abe, T. Takeguchi, *Energy Environ. Sci.*, **2015**, *8*, 1456. 3) M. Sadakiyo, S. Hata, X. Cui, M. Yamauchi, *Sci. Rep.* **2017**, *7*, 17032. 4) T. Fukushima, M. Yamauchi, *J. Appl. Electrochem.*, in press.

