Electrosynthesis of Amino Acids from Biomass-Derivable Acids Using Titanium Dioxide as a Catalyst

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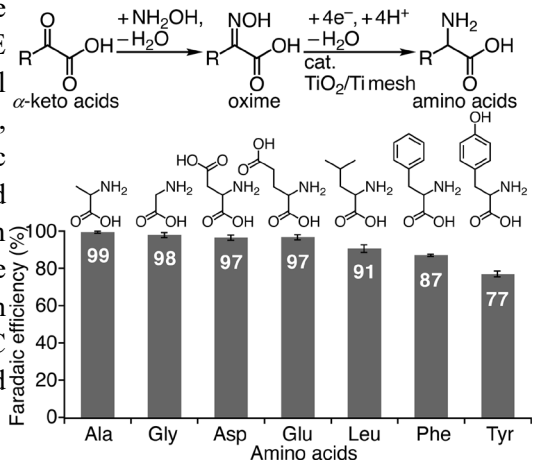
Currently, amino acids are mainly produced through the microbial fermentation process from sugar-based feedstock. However, this process has drawbacks such as high energy consumption for microbial culturing and complicated processes for product purification. The reductive amination of biomass-derivable α-keto acids is a simple and efficient way to produce amino acids, and we envisage that electrochemically driven reductive amination of α-keto acids would offer a simple and green method for amino acid synthesis, because the electrochemical process can utilize water and renewable electricity as hydrogen and energy sources, respectively. Recently, we reported that a Ti mesh covered with TiO_2 (TiO_2/Ti mesh) catalyzes the electroreduction of α-keto acids to the corresponding α-hydroxyl acids.[1] We, herein, report an efficient electrocatalytic system for the reductive amination of α-keto acids on the TiO_2/Ti mesh in the presence of NH_3 or NH_2OH as the N-source to produce the corresponding amino acids. Moreover, we also present fabrication of a flow-type reactor named "polymer electrolyte amino acid electrosynthesis cell (AAEC)" and continuous electrosynthesis of alanine using it.

TiO_2/Ti mesh was prepared from Ti mesh through two-steps hydrothermal reaction (220 ºC, 12 h. in NaOH aq. and 200 ºC, 24 h in H_2O).[2] Electroreduction of pyruvic acids was performed using two-compartment electrochemical cell equipped with TiO_2/Ti mesh, Ag/AgCl electrode and Pt coil as working, reference and counter electrode, respectively. The resulting solution was analyzed by HPLC and ^{1}H NMR to estimate Faradaic efficiencies (FEs) for production of alanine and lactic acids. We optimized reaction conditions, such as applied potential, temperature, pH, pyruvic acid concentration, and N-source concentration. When NH_3 was used as a N-source, the maximum FE for alanine production was 29%. By contrast, use of NH_2OH as a N-source resulted in excellent FE of 99% for alanine production under the optimal condition. Using the similar reaction conditions, we achieved electrosynthesis of glycine, aspartic acid, glutamic acid, leucine, phenylalanine, and tyrosine from corresponding α-keto acids with remarkably high FEs of 77 – 98%.[3] The continuous electrosynthesis of alanine from pyruvic acid and NH_2OH using the AAEC equipped with TiO_2 catalyst was examined, and 77% FE for alanine production was achieved.[3]



1) T. Fukushima et al., *Sci. Technol. Adv. Mater.* **2018**, *19*, 142; M. Sadakiyo et al., *Phys. Chem. Chem. Phys.*, **2019**, *21*, 5882. 2) M. Sadakiyo et al., *Sci. Rep.* **2017**, *7*, 17032; T. Fukushima et al., *Catal. Today* in press.

3) T. Fukushima, M. Yamauchi, *Chem. Commun.* **2019**, *55*, 14721(*Inside Cover Article*).