Preparation of Cu-based nanoalloy catalysts for electrochemical nitrogen reduction reaction

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Major problems in electrochemical ammonia synthesis are low activity and selectivity with currently available electrocatalysts for N_2 reduction. In this study, Cu-based nanoalloy catalysts were synthesized and used for electrochemical nitrogen reduction reaction. As to synthesis of Cu-based nanoparticles, a typical precursor solution was prepared by mixing metal nitrates in deionized water. PH of the solution was adjusted with NaOH. Then, $N_2H_4 \cdot H_2O$ was added slowly with stirring. The obtained solution was transferred into Teflon autoclave and heated. After cooling down to room temperature, the solid product was filtered, washed and dried to yield a powder. Synthesized catalyst and Nafion solution were dispersed in a solution containing ethanol and water. After forming a homogeneous ink through sonicating, catalyst ink was loaded onto a carbon paper and dried under ambient condition.

A three-electrode configuration (working electrode: prepared catalyst electrode; counter electrode: Pt wire; reference electrode: Ag/AgCl) was used in an H-type electrochemical cell. Each compartment was filled with 0.1 M Na_2SO_4 aqueous solution. N_2 gas was bubbled into the chamber before and during the measurement. LSV (linear sweep voltammetry), CA (Chronoamperometry) and CV (cyclic voltammetry) were tested. After reduction, working electrode-side electrolyte was collected for the indophenol blue method with UV-Vis measurements for determination of produced ammonia. Catalysts were characterized with EXAFS, XRD and TEM.

Compared with previous studies, synthesized CuNi and CuZn nanoparticles did not have a better catalytic performance. However, as shown in Fig.1, Cu_1Fe_3 achieved Faradaic efficiency (2.94%) and ammonia yield rate (29.13 μg mg^{-1} cat. h^{-1}), which is better than previous study (2.43% and 20.48 μg mg^{-1} cat. h^{-1}). With Cu_1Pd_2, Faradaic efficiency (5.23%) and ammonia yield rate (24.57 μg mg^{-1} cat. h^{-1}) were obtained. Meanwhile, Faradaic efficiency of Cu_2Pd_1 reached 3.23%, with ammonia formation rate reaching 30.47 μg mg^{-1} cat. h^{-1}, which are superior to the previous studies.[1-3] It was also discovered that synthesized CuFe and CuPd nanoparticles had a better catalytic performance for electrochemical nitrogen reduction reaction than Cu, Fe and Pd pure metal nanoparticles.

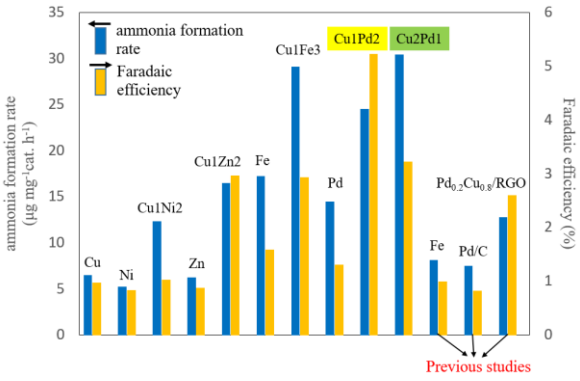

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Fig1. Ammonia formation rate and Faradaic efficiency for synthesized nanoalloy catalysts in this research