

Synthesis of Copper-Dipicolylamine Derivative Complexes and Their Electrochemical Behavior Under Carbon Dioxide

(Graduate School of Science and Technology, Meijo University) ○Kohei Nojima, Toshi Nagata

Keywords: CO₂ reduction, Cu complex, cyclic voltammetry, dipicolylamine, controlled potential electrolysis

Introduction. CO₂ reduction is expected as a technology that can reduce the amount of fossil fuel used because carbon resources can be obtained in a shorter time than biomass. Angamuthu et al¹, reported the reduction of CO₂ to oxalate using a Cu complex having a tetradentate dipicolylamine (DPA) derivative containing sulfur as a ligand. In this work, we synthesized a Cu-DPA complex and examined its electrochemical properties, in order to find out whether a similar reaction of CO₂ occurs with the tridentate complex.

Synthesis. The Cu (II) DPA complex **1** was synthesized by mixing copper perchlorate (II) hexahydrate and DPA in methanol and then stirring under reflux conditions for 4 hours (Fig. 1). The product was recrystallized from CH₃CN/tBuOMe (16% yield).

Electrochemistry. The cyclic voltammogram between -1.3V and 0V (vs. ferrocene) under N₂ showed two consecutive reduction waves at -0.35V and -0.70V. It is likely that the complex forms a dimer in a solution and the two waves correspond to the redox processes Cu₂(II,II)/Cu₂(II,I)/Cu₂(I,I). When the sweep range was widened, the reduction currents were observed at around -2.1V. The current became much larger when measured under CO₂. This large current was attributed to the reduction of the pyridine site of the complex and the reduction of CO₂ occurring at the same potential.

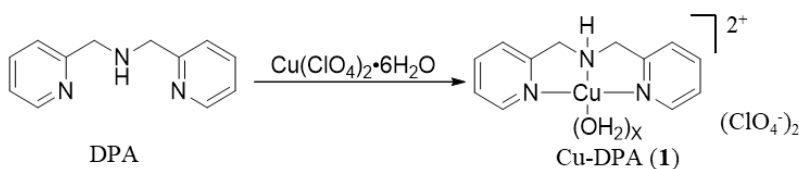


Fig.1 Synthesis of Cu(II)-DPA

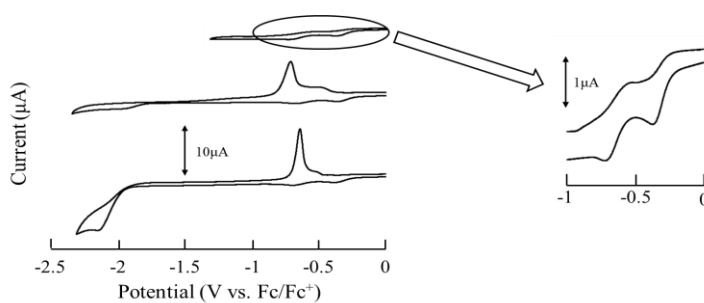


Fig.2 Voltammogram of **1**

1) R. Angamuthu, et al., *Science*, **2010**, 327, 313-315