

Electrochemical CO₂ Reduction using Metal Organic Framework (MOF)

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Increasing concentrations of atmospheric CO₂ are a consequence of rising fossil fuel combustion, a situation that confronts human civilization with unprecedented challenges like global warming and restrictions on energy consumption. As such, the development of economically feasible and environmentally benign technologies to generate electrical energy and chemical fuels is essential for a sustainable future. Among various strategies, electrochemical CO₂ reduction is one promising approach to produce hydrocarbons, alcohols, and other organic products from CO₂.¹ The major challenges that must be addressed to improve the efficiency of current electrochemical CO₂ reductions are high overpotentials, poor faradaic efficiencies, and poor product selectivities. High overpotentials and poor product selectivities derive from poorly tuned adsorption energies of critical intermediates in the reaction cycle(s), while low faradaic efficiencies are typically attributable to competitive hydrogen evolution occurring in the same range of potentials as CO₂ reduction. Improved catalysts should address these various issues. Among known homogeneous and heterogeneous electrocatalysts, metallic copper is unique for its wide range of product distribution. Unfortunately, the Cu catalyzed CO₂ reduction reaction also requires a high overpotential. However, bimetallic Cu-containing electrocatalysts, including Cu-Ni, Cu-Sn, Cu-Au, Cu-Pt, and Cu-In, have been developed for CO₂ reduction and show improved selectivity compared to pristine Cu.

Metal-organic frameworks (MOFs) comprise a class of porous, crystalline materials. MOFs show promise for a wide range of application due to their unique electronic, optical, and catalytic properties.² Recently, our experimental collaborators at Northwestern University synthesized novel heterostructures where metallic copper nanoparticles are deposited in the thin film of a water-stable MOF (NU-1000). They used solvothermal deposition in MOFs (SIM) followed by electrochemical reduction of Cu(II) to generate metallic Cu and studied electrochemical CO₂ reduction in its presence. This copper nanoparticle deposited NU-1000 was found to exhibit a promising catalytic efficiency towards electrochemical reduction of CO₂ in an aqueous electrolyte.³ Interestingly, our collaborators have also found that copper-indium nanoparticles deposited in NU-1000 exhibit better product selectivity in aqueous electrolyte compared to pure Cu or In. More specifically, methanol is obtained as a major product at an applied potential of -0.82 V with respect to the reversible hydrogen electrode.

Our goal is to use theory to elucidate the mechanistic details of electrochemical CO₂ reduction taking place on Cu and Cu-In nanoparticles embedded in NU-1000. Cluster and periodic calculations should shed light on key atomistic details, electronic factors, steric, and strain energies that dictate overall thermochemistry, kinetics, and finally product selectivity. Insights won from fundamental studies should help both experimentalists and theorists to design improved MOF-based electrocatalysts for efficient electrochemical CO₂ reduction.

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2. Majewski, et. al.; ACS Energy Lett. 2018, 3, 598–611.
3. Kung, C.-W. et. al.; ACS Energy Lett. 2017, 2, 2394–2401.