

Mechanisms of molecular catalysis of CO₂ and O₂ electroreduction with metalloporphyrins.

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Solar-driven electrochemical splitting of water to molecular hydrogen and oxygen, along with the reduction of carbon dioxide are small molecule transformations that hold promise as routes of storing sunlight in energy-dense chemical bonds. Activation penalties require the help of catalysts, usually transition metal derivatives.

We will provide the basic principles of molecular catalysis of electrochemical reactions based on the use of cyclic voltammetry as an analytical tool. Two examples will be discussed in details: (i) catalysis of the CO₂-to-CO conversion with iron porphyrins to illustrate how mechanism analysis can lead to an intelligent design of a catalyst; (ii) catalysis of the O₂-to-H₂O conversion with manganese porphyrins showing the crucial role of proton couple electron transfer (PCET) in the process