MOLECULAR COPPER CATALYSTS FOR SUSTAINABLE AND EFFICIENT H_2O_2 PRODUCTION

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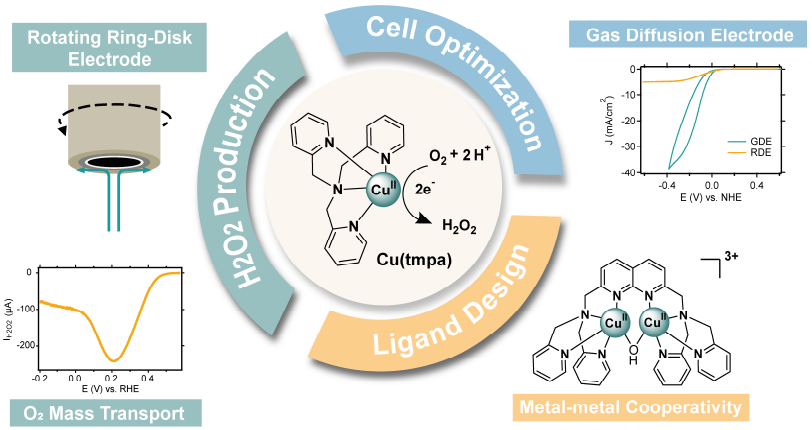
Hydrogen peroxide is a bulk chemical that is currently produced by the energy-intensive anthraquinone process. As an alternative, H_2O_2 can be produced in a sustainable pathway via the two-electron reduction of O_2. In nature, oxygen is efficiently reduced at the copper-based active site of multicopper oxidases. Inspired by the excellent activity of these enzymes,[1] we present the use of molecular copper complexes for the production of H_2O_2 via the electrochemical oxygen reduction reaction (ORR).

Recently, we reported the mononuclear copper-based pyridylalkylamine complex Cu(tmpa) to be a record-breaking ORR catalyst, doing over a million turnovers per second.[2] In this talk, we show that this complex can be used in bulk electrolysis to produce H_2O_2. More specifically, good efficiencies to H_2O_2 can be obtained by optimization of the mass transport of oxygen. We show that Cu(tmpa) can produce aqueous H_2O_2 solutions while retaining its activity over 8 hours with a faradaic efficiency to H_2O_2 of > 50%.

Furthermore, we will present how modification of the pyridylalkylamine-type ligand can be used to generate the dinuclear variant of Cu(tmpa). As a result, we have shown that in this dinuclear system metal-metal cooperativity plays a key role and the reaction mechanism differs from the mononuclear analogue.[3] To conclude, strategies on how to optimize the electrochemical cell design are presented. Moving from conventional, stationary and rotating disk setups, to gas diffusion electrodes in flow systems, we will show how the cell design can lead to changes in the selectivity and current density to H_2O_2.



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[1] Mano, N.; Soukharev, V.; Heller, A., A Laccase-Wiring Redox Hydrogel for Efficient Catalysis of O2 Electroreduction. *J. Phys. Chem. B* **2006,** *110* 11180-11187.

[2] Langerman, M.; Hetterscheid, D. G. H., Fast Oxygen Reduction Catalyzed by a Copper(II) Tris(2-pyridylmethyl)amine Complex through a Stepwise Mechanism. *Angew. Chem. Int. Ed.* **2019,** *58* (37), 12974-12978.

[3] Langevelde, P. H. van; Kounalis, E.; Killian, L.; Monkcom, E. C.; Broere, D. L. J.; Hetterscheid, D. G. H., Mechanistic Investigations into the Selective Reduction of Oxygen by a MCO T3 Site-Inspired Dicopper Complex. *ACS Catal.* **2023**. *Accepted*