Bioelectrocatalysis for Sustainable H_2 Production by Hydrogenase Enzymes

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"Green" dihydrogen (H_2) is developing into a key player in solving the global energy crisis and reducing CO_2 emissions, as its combustion only produces water as a side product. However, current technologies for producing, transporting and storing "green" hydrogen are somewhat limited and more than 99% of globally utilized H_2 are still tracked back to fossil fuels and thus considered to be economically unfriendly.[1] In order to access more sustainable hydrogen evolution technologies, the enzyme class of hydrogenases can act as a blueprint for building ecofriendly model systems. Hydrogenases are capable of catalyzing the reversible interconversion of protons and electrons into dihydrogen with exceptional high rates at mild conditions, *i.e.* neutral pH and ambient temperature and pressure.[2]

As a model, we study the [FeFe] hydrogenase *Cp*I from the organism *Clostridium pasteurianum*, due to a relatively ease accessibility and a high bias towards hydrogen evolution (with *in vitro* TOFs of up to 5900 s^{-1}).[3] To mimic the biological environment, where electrons are delivered by oxidoreductase enzymes, the application of an electrochemical potential (that itself can be generated by renewable energy sources) to these enzymes opens a new possibility for "green" hydrogen production.[4] Herein, we present two approaches to electronically feed *Cp*I in either a direct electron transfer (DET) configuration, where the enzyme is efficiently immobilized onto a mesoporous ITO electrode, and a mediated electron transfer (MET) configuration, utilizing a electrochemically reduced low potential viologen based electron mediator.[5] The latter has shown to boost the enzymes activity beyond the so far reported activity numbers, while the former demonstrates the construction of a highly active and stable bioelectrode.

[1] IEA, *Global Hydrogen Review 2023*, IEA, Paris, **2023**.
[2] R. D. Milton, *CHIMIA*, **2024**, *78*, 13–21.
[3] M. W. Adams, *Biochim. Biophys. Acta* **1990**, *1020*, 115–145.
[4] S. Webb, R. D. Milton, *ChemElectroChem*, **2025**, *12*, e202400700.
[5] a) S. Webb, A. Veliju, P. Maroni, U.-P. Apfel, T. Happe, R. D. Milton, *Angew. Chem. Int. Ed.*, **2025**, *64*, e202416658. b) N. Ostermann, S. Webb, A. Do Nascimento Henriques, R. D. Milton, *submitted*.