Proton-coupled Electron Transfer in the Catalytic Mechanism of [FeFe]-Hydrogenase

Moritz Senger[a], Jifu Duan[b], Ulf-Peter Apfel[c], Michael Haumann[d], Sven T. Stripp[e]

[a] Department of Chemistry, Physical Chemistry,
Uppsala Universitet, 75120 Uppsala, Sweden
[b] Faculty of Biology and Biotechnology, Photobiotechnology,
Ruhr-Universität Bochum, 44801 Bochum, Germany
[c] Faculty of Chemistry and Biochemistry, Small Molecule Activation,
Ruhr-Universität Bochum, 44801 Bochum, Germany
[d] Department of Physics, Biophysics of Metalloenzymes,
Freie Universität Berlin, 14195 Berlin, Germany
[f] Department of Physics, Experimental Molecular Biophysics,
Freie Universität Berlin, 14195 Berlin, Germany

sven.stripp@fu-berlin.de

Hydrogenases are iron-sulfur enzymes that catalyze hydrogen turnover ($2H^+ + 2e^- \leftrightarrow H_2$) with unrivaled efficiency.[1] Reported TOFs are up to 20k H_2 s^{-1} at pH 7 and 24°C without significant overpotential (*i.e.*, -420 mV vs SHE). Hydrogenase are bioinorganic model systems and inspired a great wealth of synthetic complexes that mimic the bimetallic active site cofactor of [NiFe]- or [FeFe]-hydrogenases. While the catalytic mechanism of the former is considered understood[2], the inner workings of [FeFe]-hydrogenase are subject to controversial discussion.[3]

Based on *in situ* infrared spectroscopy[4,5] of the catalytic 'H-cluster' -- the unique [4Fe-4S]–[FeFe]$(CO)_3(CN^-)_2$ cluster of [FeFe]-hydrogenases -- I will introduce the key ideas of biological hydrogen turnover. This involves the formation of a low-valent metal-hydride species[6], site-selective proton transfer[7], and proton-coupled electron transfer (PCET). I will outline the key differences in the models that have been put forward explaining [FeFe]-hydrogenase catalysis and discuss the implications for biomimetic chemistry.[8]

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