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Frontiers in Catalysis Science and Engineering
Seminar Series

Elucidating Structure and Function of [NiFe] and [FeFe] Hydrogenases by Spectroscopic and Electrochemical Techniques

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Hydrogenases catalyze the reversible heterolytic splitting of H_2 at binuclear (NiFe or FeFe) metal centers. Understanding how these enzymes achieve their high efficiencies is key to developing molecular catalysts for H_2 conversion and production. To shed light on the catalytic cycles of these enzymes intermediates are trapped and characterized by electrochemical and spectroscopic methods, using mostly vibrational and magnetic resonance techniques. The obtained parameters are verified by DFT calculations. The [NiFe] hydrogenases are quite well understood; important results are briefly reviewed. The field of [FeFe] hydrogenases has recently been revolutionized by the discovery of artificial maturation. The focus of this lecture will therefore be on these enzymes. The active site of [FeFe] hydrogenase (the "H-cluster") is composed of a classical [4Fe-4S] cluster linked via a cysteine to a [2Fe] center that carries CO and CN^- ligands, and a bridging azadithiolate (adt) ligand. For [FeFe] hydrogenases from several organisms artificial maturation of the enzymes has been described, where the apo-protein carrying only the [4Fe-4S] cluster is reacted with chemically synthesized [2Fe] clusters. Such clusters with different substituents, different atomic compositions, and even different metals have been incorporated. The technique also allows specific isotope labelling, e.g. with ^{57}Fe, ^{13}C, ^{15}N and ^{2}H nuclei. This approach enabled the direct detection of an iron-bound terminal hydride in the reduced state of the enzyme, using nuclear resonance vibrational spectroscopy (NRVS), supported by NMR in solution studies. IR spectroelectrochemistry at different pH values allowed the detection of further intermediates, demonstrating the importance of proton coupled electron transfer in the enzymatic cycle. Experiments showing how the interaction of the H-cluster with neighboring iron-sulfur centers influences the efficiency of the hydrogenase are presented. The oxygen sensitivity of these enzymes is discussed that can significantly be improved by embedding the [FeFe] hydrogenase in a tailor-made polymer matrix. It is demonstrated that hydrogenases and related model systems can successfully be attached to electrodes and used in devices.

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