[NiFe]hydrogenase Running the Reactions between H_2 and O_2 Molecules

Ki-Seok Yoon[1,2,3]

[1] International Institute for Carbon-Neutral Energy Research, Kyushu University;
[2] Dept. of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University;
[3] Centre for Small Molecule Energy, Graduate School of Engineering, Kyushu University;
744 Moto-oka, Nishi-ku, Fukuoka 819-0395, Japan

E-mail: yoon@i2cner.kyushu-u.ac.jp

The biological H_2 activation is an important process to modulate the redox balance of energy metabolism in living cells by H_2-oxidation and H_2-production. [NiFe]hydrogenases catalyze the reversible reaction of the cleavage and production of H_2, harboring a NiFe center for H_2 activation in a large subunit and iron-sulfur clusters for electron transfer in a small subunit. Due to its high catalytic ability for H_2-activation, [NiFe]hydrogenases have received much attention as their potential catalysts in many H_2-based technologies. However, most hydrogenases found in microorganisms are highly sensitive to O_2, leading to inactivation of catalytic activity after air oxidation.

Within the course of research projects, we have found a number of new O_2-tolerant [NiFe]hydrogenases from Knallgas bacteria[1-3], such as membrane-bound [NiFe] hydrogenase (MBH) and soluble NAD^+-reducing [NiFe]hydrogenase (SH). The structural analysis of the newly found species reveals the special features of a proximal iron-sulfur cluster to protect the [NiFe]-active site against oxidative stress. The O_2-tolerant MBH from hydrogen-oxidizing bacteria contains a novel iron-sulfur cluster in a small subunit, which plays an essential role in the O_2-tolerant mechanism. On the other hand, SH localized in the cytosol has a unique intra-molecular system of protein complex, which functions as a redox sensor to protect the NiFe center by attacking O_2 molecule. However, the catalytic activity of O_2-tolerant [NiFe]hydrogenases is lower than those of O_2-sensitive [NiFe]hydrogenases. In our studies in I^2CNER, we explored other distinct hydrogenase possessing both abilities of high O_2-tolerance and H_2-activation[4-6]. A newly discovered [NiFe]hydrogenase from our isolated *Citrobacter* sp. S-77 (MBH-S77) displays an excellent performance for H_2-oxidation and O_2-tolerance. Most significantly, the catalytic H_2-activation of MBH-S77 surpasses that of platinum in polymer electrolyte fuel cell as an anode catalyst. Intriguingly, our most recent studies have revealed that an amino acid near a proximal [4Fe-4S] cluster plays a key role in its catalytic activity for H_2-oxidation and O_2-tolerance. On the basis of our recent findings, I will present the structural and functional insights into the biological H_2-activation of [NiFe]hydrogenases adaptation to aerobic conditions.

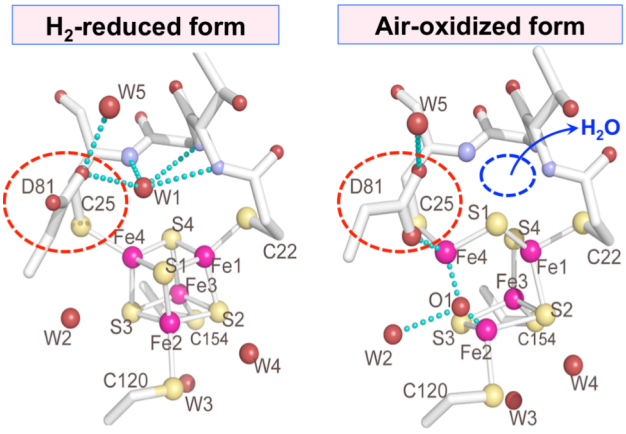

Figure 1. Redox-dependent structural changes of a proximal [4Fe-4S] cluster of MBH-S77 by Asp81.

References

[1] Yoon K.-S., *et al.*, *Int. J. Hydrogen Energy.*, **36**, 7081 (2011); [2] Shomura Y., *et al.*, *Nature*, **479**, 253 (2011); [3] Shomura Y., *et al.*, *Science*, **537**, 928 (2017); [4] Eguchi, S., *et al., J. Biosci. Bioeng.* 114, 479 (2012); [5] Matsumoto T., *et al.*, *Angew. Chem. Int. Ed.*, 53, 8895 (2014); [6] Noor D.M.D., *et al.*, *Chem. Commun.*, 54, 12485 (2018).