

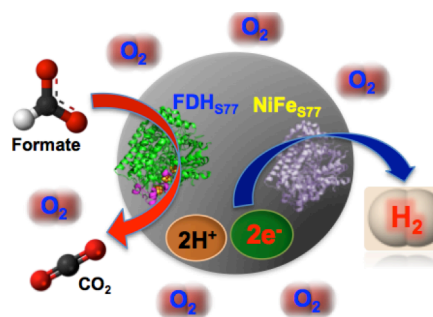
CO₂-hydrogenation into formate by the membrane-bound enzyme complex

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H₂ is an effective energy carrier with a high energy density per molecule. Therefore, we are particularly interested in the biochemical reaction of H₂-dependent reduction of CO₂ into formate, because formate is greenhouse gas sequestration and can easily store energy as a renewable liquid hydrogen energy carrier. However, most biocatalysts to perform CO₂-hydrogenation are highly O₂-sensitive, which is a bottleneck for biotechnical application. To resolve this difficult issue, we have found a number of new O₂-stable [NiFe]hydrogenases and determined the structural basis for the catalytic mechanism of H₂ and O₂ molecules¹⁻³.

In this study, we constructed an efficient system for H₂-dependent CO₂ reduction into formate using the immobilized bacterial membrane on carbon black. Because a [Mo]-formate dehydrogenase (FDH_{S77}) and a [NiFe]-hydrogenase (NiFe_{S77}) from our isolated bacterium *Citrobacter* sp. S-77 displayed high catalytic activity with remarkable O₂-stability^{4,5}. In fact, the fabricated polymer electrolyte fuel cell (PEFC) using the purified NiFe_{S77} as an anode catalyst, displaying its power density over 647-times superior for H₂-oxidation than that of a platinum catalyst in the PEFC⁶. Intriguingly, our recent



Scheme 1. Biochemical system for the reversible reaction of H₂-dependent CO₂ reduction into formate by an immobilized bacterial enzymes onto carbon black.

structural analysis revealed that an amino acid of Asp81 near a proximal [4Fe-4S] cluster plays a key role in its catalytic activity for H₂-oxidation and O₂-tolerance⁷. The immobilized FDH_{S77} and NiFe_{S77} onto carbon black lead to elevate the reversible activity for H₂ production from formate and H₂-dependent CO₂ reduction into formate (**Scheme 1**). Notably, the H₂ production can occur even in the presence of air environment. To our future studies, we will construct a high efficiency biological system for CO₂-hydrogenation into formate by the homogeneously purified FDH_{S77} and NiFe_{S77} immobilized onto carbon black. On the basis of our findings, I will present the structural and functional insights into the biochemical CO₂-hydrogenation into formate with robust biocatalysts for Carbon-Neutral Energy Research.

References worked by author;

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