

# Electrochemical studies of CO<sub>2</sub>-reducing enzymes

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Only two metalloenzymes are able to reduce directly CO<sub>2</sub>: the NiFe CO dehydrogenase, which reduces CO<sub>2</sub> to CO, and the Mo/W formate dehydrogenase, which produces formate. These enzymes are fast, energy efficient and highly specific in terms of product, hence the interest to understand their catalytic mechanism and the origin of their catalytic performances. They can readily be connected to electrodes, so we have used Protein Film Electrochemistry<sup>1</sup> to learn about various aspects of their reactivity. We have demonstrated that the form of “CO<sub>2</sub>” being reduced is really CO<sub>2</sub> (as opposed to HCO<sub>3</sub><sup>-</sup>) both for formate dehydrogenases and CO dehydrogenases<sup>2</sup>, and that the CO dehydrogenases, despite having high sequence similarities, have very different properties in the reaction with their substrates and inhibitors<sup>3,4</sup>.

Regarding formate dehydrogenases, according to the current consensus, the metal ion of the catalytic center in its active form is coordinated by 6 S (or 5 S and 1 Se) atoms, leaving no free coordination site to which formate could bind to the metal<sup>5</sup>. Some authors have proposed that one of the active site ligands decoordinates during turnover to allow formate binding, while another proposal is that the oxidation of formate takes place in the second coordination sphere of the metal. The analysis of our electrochemical data, obtained on two different formate dehydrogenases, strongly support the “second coordination sphere” hypothesis<sup>6</sup>, showing that formate likely does not bind to the metal of the active site.

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