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Review article

Molybdenum and tungsten-containing formate dehydrogenases: Aiming to inspire a catalyst for carbon dioxide utilization

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ABSTRACT

The global energy demand and the present high dependence on fossil fuels have caused an unprecedented increase in the Earth's atmosphere carbon dioxide concentration. Its exponential and uncontrollable rise is responsible for large and unpredictable impacts on the world climate and for ocean acidification, thus, being a major concern for the ecosystems and human's daily life. On the other hand, the carbon dioxide abundance and low cost make it an interesting source for the production of chemical feedstocks and fuels. Yet, the thermodynamic and kinetic stability of the carbon dioxide molecule makes its utilization a laboratorial/industrially challenging task.

In this Review, we propose to use the molybdenum and tungsten-containing formate dehydrogenase (FDH) enzymes as a model to understand the mechanistic strategies and key chemical features needed to reduce carbon dioxide to formate. We will highlight the present knowledge about the structure of FDHs, with particular emphasis on active site features, reaction mechanism and ability to reduce carbon dioxide to formate. The information gathered aims to inspire the development of new efficient (bio)catalysts for the atmospheric carbon dioxide utilization, to produce energy and chemical feedstocks, while reducing an important environmental pollutant.

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Abbreviations: EPR, electron paramagnetic resonance spectroscopy; FDH, formate dehydrogenase; M, metal (refers to molybdenum and/or tungsten); Mo-FDH, molybdenum-containing formate dehydrogenase; W-FDH, tungsten-containing formate dehydrogenase; XAS, X-ray absorption spectroscopy.

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Isabel Moura *received her Degree in Chemical Engineering from Technical University of Lisbon (Pt) in 1974. She received her Masters in Physical Inorganic Chemistry in 1977 and her Ph.D. from New University of Lisbon (UNL) in 1981 on the thesis entitled "Characterization of two types of iron sulfur centers in two proteins isolated from Desulfovibrio gigas". Since then she was an Assistant Professor until 1981 in the UNL. In 1986 she became an Associate Professor at UNL. She has done the habilitation in 1994 and became a Full Professor in 1997 at UNL. During her career she was a Visiting Professor in University of Geogia, Athens, USA. During the period 2000/2011 she was the Head of the Chemistry Department of FCT/UNL and the Director of the Associated Laboratory REQUIMTE for Sustainable Chemistry. Scientific interests: The main work aims on the study of Structure-Function of Metalloproteins. Application of biochemical and spectroscopic tools (NMR, EPR and Mössbauer). Proteins involved in relevant bacterial metabolic pathways – N and S Biocycles. Active sites include Cu, Co, hemes, iron-sulfur centers (rubredoxin type, [2Fe-4S], [3Fe-4S], [4Fe-4S]) as well as association of Fe-S centers with Mo, W, Ni, siroheme and flavins. New type of clusters and new metal associations is also one of the main topics of research. More than 385 publications, h-index of 56.*

José J. G. Moura *has a degree in Chemical Engineering and a Ph.D. in Chemistry, Professor of Chemistry at the Department of Chemistry, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa. The main field of research is Bioinorganic Chemistry and the role of Metals in Biology. More than 400 articles indexed in ISI Web of Knowledge and an h-index of 57. For extended periods Research Specialist at UMinnesota (US) and Adjunct Professor at UGeorgia, Athens (US). Past President of Chemistry Department and of Scientific Council at FCT-UNL, Portuguese Delegate to COST and INTAS, a member of Scientific Panel in the Calouste Gulbenkian Foundation and FCT/MCTES, NSF (US) Specialized Panel, and of several scientific editorial boards. In 2006, he was elected Member of Academia das Ciências de Lisboa and in 2010, elected President of the Society of Biological Inorganic Chemistry, for 2 years. Scientific key words: Bioinorganic, Biophysics, Biocatalysis, Energy Bioconversion (Hydrogen), Role of metals in Biology (heme and non-heme iron, molybdenum, tungsten, nickel, copper, vanadium and cobalt), Inorganic systems as models for biocatalysis, Spectroscopy (NMR, EPR and Mössbauer), (Bio) Electrochemistry, Protein-Protein interactions. Other interests: Director of FCT-UNL Campus FCT Library and Department of Documentation and Culture. Culture/Scientific Interfaces. Multidisciplinary curator activities (Art and Science).*

Contents

1. The "carbon dioxide crisis

The global energy demand and the present high dependence on fossil fuels have caused the increase in the atmospheric carbon dioxide concentration for the highest values since records began [1]. Due to its significant green-house effect, carbon dioxide rise is responsible for large and unpredictable impacts on the world climate, besides being responsible for ocean warming and acidification (its major sink) [2,3]. While some authors defend that these alterations are no longer reversible, the carbon dioxide emissions must be greatly decelerate. Future energy sources should be carbon-neutral and based on solar, wind and geothermal energy and new methods to store, transport and use "on demand" the energy from these sources must be developed.

One solution to control the "carbon dioxide crisis" (alongside all other efforts to reduce emissions) would be the use of a renewable energy to scavenge the atmospheric carbon dioxide and convert it back into fuel [4]. Certainly, the carbon dioxide abundance makes it an attractive source for the production of fuels and other synthetic value-added chemicals and there is a huge interest in the development of strategies to efficiently scavenge and activate the atmospheric carbon dioxide [1,5–8]. One of the major challenges is the thermodynamic and kinetic stability of the carbon dioxide molecule that makes its laboratory/industrial activation a very difficult task. Nature, on the contrary, has found several different strategies to activate and use carbon dioxide [9–12], applying different chemical approaches, with specific enzymes, to cleave the C—O bond (reduction to carbon monoxide) and form C—C (*e.g.*, addition to ribulose 1,5-bisphosphate) and C—H bonds (reduction to formate) [8–14]. Understanding the chemical strategies already tested and proved by Nature (reaction mechanisms and key chemical features) would certainly contribute to the development of new efficient (bio)catalysts for the atmospheric carbon dioxide utilization [1,8,15–21].

This Review will be focused on the carbon dioxide reduction to formate catalyzed by formate dehydrogenase (FDH) enzymes. Formate is an interesting carbon dioxide product for several reasons: it is the first (and stable) intermediate in the reduction of carbon dioxide to methanol or methane; it is used as a chemical building block in industry; it is a viable energy source, easier to store and transport than dihydrogen (formate and dihydrogen are oxidized at similar potentials) and fuel cells that use formate are being developed. All these positive outcomes make worthwhile systematic investigations to develop more efficient (bio)catalysts

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