

Preface

There is a general consensus in considering the use of fossil fuels (petroleum, natural gas and coal) as the cause of serious environmental problems. Because the amount of energy derived from these fossil reserves is close to 80 % of the entire World's energy consumption, there is a pressing need of new, non-polluting and renewable energy sources (Report of the International Energy Agency, 2010). Although hydrogen (H_2) is not a primary energy source, it has been considered a promising alternative to fossil fuels. By definition, an energy source is such only if useful energy can be directly extracted or recovered from it; in this respect, H_2 is an "energy carrier" as it is derived from an energy reservoir and it can be used, like electricity, for the "transport" of energy from the production site to the sites of its use. The main consequence of this feature is that hydrogen can be produced only by consuming primary energy sources, which at the moment are mainly fossil fuels. However, there are at least two properties making the use of hydrogen quite attractive, namely: its large presence in nature, even if usually linked with other atoms, e.g. with oxygen in water or with oxygen, carbon and other elements in organic compounds, and the possibility to use it without releasing pollutants or greenhouse gases (GHGs) in the atmosphere. Interestingly, hydrogen can also be produced by exploiting the metabolic features of several microorganisms in a carbon neutral process that has been called "biological hydrogen production". Bio-hydrogen production is also characterized by important advantages over the thermochemical and electrochemical techniques currently utilized or under study. Indeed, microbiological processes can produce hydrogen using renewable resources, in carbon neutral processes operating at room temperature and pressure, and with low environmental impact. A negative aspect of the

microbial hydrogen production in natural habitats is the fact that although a large number of bacteria, belonging to different taxonomic groups, possess the capability to produce hydrogen, free hydrogen of biological origin can hardly be captured in nature because hydrogen-producing and hydrogen-consuming microorganisms live in the same natural environments.

Bio-hydrogen production has been known for almost a century and research directed at applying this process to a practical means of hydrogen fuel production has been carried out for over a quarter of a century. A milestone in bio-hydrogen research was the observation by Hans Gaffron, while working at the University of Chicago in 1939, that algae can generate hydrogen by both fermentation and photochemistry (H. Gaffron (1939) Reduction of CO_2 with H_2 in green plants. *Nature* 143:204–205). Ten years later, Gest and Kamen (H. Gest and M.D. Kamen (1949) Photoproduction of molecular hydrogen by *Rhodospirillum rubrum*. *Science* 109: 558–559) discovered the light-dependent production of hydrogen in parallel to nitrogen fixation by the facultative photosynthetic bacterium *Rhodospirillum rubrum*. Notably, in "Memoir of a 1949 railway journey with photosynthetic bacteria" (Photosynthesis Res 61: 91–96), H. Gest (1999) commented on this discovery as "A serendipic observation at the Hopkins Marine Station of Stanford University in 1948 led to the discovery that anoxygenic photosynthetic bacteria can fix molecular nitrogen ... and generate hydrogen". One of us (Zannoni D), while working as an associate researcher at the St. Louis University Medical School in 1978, was fortunate enough to have known personally H. Gest, Professor of Microbiology at the University of Bloomington (Indiana). He remembers that they had a long discussion on the way to define what it is now recognized as the "accessory oxidant-dependent

fermentation in photosynthetic bacteria” (See: *The Phototrophic Bacteria: Anaerobic Life in the Light*, J.G. Ormerod Ed., 1983, vol 4, University of California Press, Blackwell Sc. Pub.). Enormous advances have been made since then on genetics, biochemistry, and biotechnological applications of photosynthetic bacteria and the present book, entitled *Microbial BioEnergy: Hydrogen Production* is a compendium overviewing most of the processes important for the microbial hydrogen production including bacterial hydrogen photo-generation.

The book begins with a chapter on bioenergy from microorganisms describing some of the challenges in meeting future energy needs in order to address climate changes through the development of bioenergy (Chap. 1). Critical factors in mature technologies and future directions in nascent technologies are also reviewed. The volume includes a section (Chaps. 2, 3, 4, and 5) covering structural, molecular, and functional aspects of hydrogenases as efficient biological catalysts for the production of molecular hydrogen and, consequently, its oxidation a way to get rid of the excess reducing power in cyanobacteria and green algae. As cyanobacteria are unique organisms that accommodate both oxygenic photosynthesis and nitrogen fixation, they are extensively covered in Chap. 6 with respect to their production of ammonium concomitantly with hydrogen formation. Solar energy is also used by photosynthetic purple non-sulfur bacteria to generate hydrogen gas from organic sources via the enzyme nitrogenase. Chapter 7 focuses on the advances that have been made in hydrogen generation through the use of systems biology approaches such as genomics, transcriptomics and ^{13}C -fluxomics in *Rhodospseudomonas palustris* CGA009. Chapters 8 and 9 cover two emerging research fields in hydrogen production: the use of thermophilic and hyperthermophilic microorganisms of the genera *Caldicellulosiruptor* and *Thermotoga*. As these genera utilize an extraordinary array of substrates that are converted by dark-fermentation to hydrogen at efficiencies approaching the “Thauer limit” of 4 mol H_2 /mol glucose, the availabil-

ity of several genome sequences and their metabolic features open new perspectives for biohydrogen generation. Bioelectrochemical systems coupled to indirect hydrogen production are reviewed in Chap. 8. These systems are not subjected to the hydrogen yield constraints and have been proven to work with any biodegradable organic substrate. Chapters 11, 12, 13, and 14 are mostly dedicated to photobioreactors using purple non-sulfur bacteria and microalgae. This section of the book examines in detail how hydrogen production depends on various kinds of organic wastes, on the photosynthetic efficiency and light distribution. The basic principles for designing photobioreactors in mass culture for biofuel are also examined along with the advantages and limitations of immobilized cell-systems for hydrogen photoproduction. The volume ends with a chapter (Chap. 15) dealing with the unconventional concept that if hydrogen is used as an energy carrier, there are consistent benefits to be expected, depending on how hydrogen is generated. The existing technical problems lying ahead for the creation of an apparent “Hydrogen Based Society” are examined and it is concluded that they will be solved within a reasonable period of time.

Following the suggestion of the Series editors, Govindjee and Tom Sharkey, we are deeply honored to dedicate this book to Hans Gaffron (1902–1979) and Howard Gest (1921–2012).

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