Hydrogen: An Overview

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Bill Tumas received a B.A. in chemistry from Ithaca College in 1980 and a Ph.D. in chemistry from Stanford University in 1985. After postdoctoral research at Caltech, he worked for six years at Dupont Central Research in Wilmington, DE, before moving to Los Alamos National Laboratory in 1993, where he has been a Group Leader, a Program Manager, the Director of the Los Alamos Institute for Hydrogen and Fuel Cell Research, and the lead principal investigator of the U.S. Department of Energy Center of Excellence for Chemical Hydrogen Storage. He is currently the Program Directory for Alternative Energy and Infrastructure at Los Alamos, where he is responsible for programs in hydrogen and fuel cells, renewable energy, and energy efficiency.

Providing an abundant, clean, and secure renewable energy source is one of the key technological challenges facing mankind. Resurgence in the chemistry and biochemistry of hydrogen, the world's simplest closed-shell molecule, has been spurred by recent scientific and technological interest in hydrogen as an energy carrier and potential transportation fuel. Our current energy infrastructure is dominated by fossil fuel use, which leads to greenhouse gas emissions. Hydrogen is potentially an ideal energy carrier, as it is nonpolluting and gives up both its electrons upon oxidation to form only water. Although it is the most abundant element in the universe, elemental hydrogen is not present in great quantities on earth. A number of key challenges must be overcome for hydrogen to be used broadly in a sustainable future energy infrastructure to solve the globe's energy problems. To accrue the full environmental benefit of hydrogen as an energy carrier, low-carbon intensive, low polluting, and lower cost processes for producing hydrogen from renewable energy sources need to be developed. Scientific advances are needed to develop more energy efficient and cost-effective methods for purification and delivery, to design higher energy density hydrogen storage systems, especially for vehicular on-board storage, and to enable more durable fuel cells for converting hydrogen into electrical energy. Governments and industries, particularly in the United States, Japan, and Europe, have been investing heavily in research and development to overcome the technical barriers for hydrogen production, storage, and utilization to enable a sustainable future energy infrastructure based on hydrogen.

Globally, industry already produces and uses hydrogen on a massive scale. A plethora of catalysts and catalytic processes involving hydrogen have been developed, ranging from the synthesis of ammonia to asymmetric hydrogenation processes for pharmaceuticals. The current platforms for hydrogen production are largely based on fossil fuels, are relatively energy inefficient, and lead to the emission of significant quantities of greenhouse gases. Nature has developed its own set of catalysts to produce hydrogen or to utilize it as an energy source—the hydrogenases. The genesis of the hydrogenase enzymes probably occurred during the early stages of life on our planet, when the earth had a hydrogen-rich atmosphere and the existing primitive organisms relied on this molecule as an energy source. The enzyme is found in many microorganisms, in particular in archaea and bacteria, but also in some eukaryotes. Three phylogenically distinct classes of hydrogenases are known today. These are the [NiFe]-, the [FeFe]-, and the [Fe]-hydrogenases. The first two classes contain binuclear metal cores with an unusual ligand sphere as catalytic centers, whereas the third class harbors a mononuclear iron next to a special organic cofactor. Nature's concept of hydrogen conversion—or the reverse process of hydrogen generation—is based on heterolytic splitting of dihydrogen ($H_2 \rightleftharpoons H^+ + H^-$) at highly optimized catalytic centers. The acidity of H_2, which is extremely low, is dramatically increased by binding to a metal. While Nature's catalysts are based on first row transition metals, many of the catalysts used for anthropogenic production and utilization of hydrogen involve precious metals such as platinum. However, the

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situation continues to improve as new catalysts, including biomimetic systems, are being developed.

This thematic issue on Hydrogen aims to capture the excitement of recent advances in hydrogen production, storage, and utilization by providing a broad overview of the current state of our scientific understanding of the pertinent chemistry and biochemistry. The biological generation and utilization of hydrogen in nature where the enzyme hydrogenase plays the central role is also reviewed in this issue. One common theme among the articles presented herein is the understanding and control of the interactions and reactions of hydrogen at transition metal centers. A wide range of experimental and theoretical tools have been applied to interrogate, characterize, and even design catalytic systems. We could not possibly capture all the advances and aspects of the scientific challenges in a single issue, but we believe that the cross section provided by the review articles will be of interest to a broad audience.

Polymer electrolyte membrane (PEM) fuel cells are being developed as hydrogen-based electrical power sources at a range of scales for transportation and stationary and portable power applications. Fuel cells are remarkably efficient in converting hydrogen to water and electrical energy, and significant advances have been made in fuel cell technology. Widespread use and commercialization will, however, require improvements in fuel cell lifetime and durability, which are also directly related to overall costs. In their article on “Scientific Aspects of Polymer Electrolyte Fuel Cell Durability and Degradation”, Borup *et al.* provide a critical review of the chemical mechanisms and processes involved in fuel cell degradation and durability, an area of research that has recently received considerable attention. This review stems directly from the contributing authors’ participation in a 2006 workshop on fuel cell degradation, jointly hosted by Los Alamos National Laboratory, Japan’s New Energy and Industrial Technology Development Organization, and National Institute for Advanced Industrial Science and Technology in Santa Fe, NM. Within PEM fuel cells, the electrocatalysts and supports, membranes, and other components are exposed to an aggressive chemical environment of strongly oxidizing and highly acidic conditions, high temperature, high electrochemical potentials and gradients, and reactive chemical intermediates. Methods for durability testing and the effects of operating conditions on fuel cell performance are reviewed along with the experimental methods and recent results in probing and understanding the chemical aspects of internal component durability, particularly membrane degradation and electrocatalyst stability.

Navarro, Peña, and Fierro provide a comprehensive review of hydrogen production from catalytic processing of fossil fuels and biomass in “Hydrogen Production Reactions from Carbon Feedstocks: Fossil Fuels and Biomass”. While a future energy infrastructure based on hydrogen will require generation of hydrogen from renewable energy sources to accrue the desired environmental benefits, production from fossil fuels will continue to play an important role in at least the next decade. A range of chemical and catalytic processes for production from fossil fuels are examined including reforming and catalytic partial oxidation of methane and liquid hydrocarbons. Processes that have the potential to avoid the production of carbon dioxide as a coproduct are also surveyed. The use of renewable biomass-derived carbon-based sources for hydrogen production is an attractive alternative to fossil fuels, as it could be much less carbon dioxide intensive. Progress in gasification and reforming is reviewed along with other processes for biomass conversion.

As described by Palo, Dagle, and Holladay in their article “Methanol Steam Reforming for Hydrogen Production”, there is considerable interest in methanol as a source of hydrogen for fuel cell applications. Methanol contains significant amounts of hydrogen and can be activated to produce elemental hydrogen at lower temperatures than other conventional carbon-based fuels. Palo et al. provide an overview of methanol steam reforming, with a focus on catalyst development and mechanistic aspects as well as reactor and system development. The progress in catalysts based on copper and on group VIII metals (Ni, Pd, Pt) and their alloys is surveyed. Particular focus is placed on microreactor development for portable power applications.

The production of hydrogen using renewable solar energy represents an ideal method for sustainable energy production and storage. In “Hydrogen Production by Molecular Photocatalysis”, Esswein and Nocera review the current state of photocatalytic hydrogen production using discrete homogeneous molecular transition metal catalysts. To overcome thermodynamic barriers associated with one-electron reduction pathways, it is imperative to develop catalytic systems that use two-electron reduction pathways such as multielectron reduction processes or proton-coupled electron transfer. A range of inner sphere mechanisms involving bond cleavage in the dehydrogenation reactions of alkanes and alcohols by a range of transition metal based catalysts is examined. Reactions of photoexcited states of transition metal complexes with acids are also surveyed along with a review of current approaches involving three component systems comprised of a light absorber, a proton reduction catalysts, and an electron relay system. The latter systems typically rely on outer sphere electron transfer mechanisms. Carbon dioxide reduction and the molecular aspects of photobiological systems are discussed as well. The authors point out that significant progress has been made in our understanding of the primary chemical and photochemical processes, but new systems and design strategies will likely be needed to overcome the fundamental challenges of efficient hydrogen generation.

Harnessing the thermal energy of the sun’s irradiation through solar concentration and high temperature thermochemical cycles offers another alternative for renewable and sustainable hydrogen production. Kodama and Gokon’s article “Thermochemical Cycles for High-Temperature Solar Hydrogen Production” provides a review of cycles that are driven at high temperature to provide the net effect of splitting of water into hydrogen and oxygen in distinct steps. Two-step and multistep processes are surveyed along with the current development status of specific processes and reactors. Simple two-step processes typically require higher temperatures than multistep processes, which can operate below 1200 K. Emphasis is placed on those systems which show promise for development and application.

Energy efficient processes for hydrogen production and utilization will require cost-effective and energy efficient methods for separation and purification. “Membranes for Hydrogen Separation” are examined by Ockwig and Nenoff. Membrane separation is promising due to the potential for continuous, energy efficient processes. A wide range of materials are currently under investigation for membrane separations, including metals and alloys, silica, zeolites, carbon, polymers, and composites. The composition, properties, and performance of these materials is reviewed along with progress in this burgeoning field.

Despite its high gravimetric energy density, hydrogen, even in liquid form, has a low volumetric energy density compared to other transportation fuels, so on-board storage of hydrogen remains a critical technical barrier to widespread hydrogen-based transportation. Orimo, Nakamori, Eliseo, Züttel, and Jensen review the synthesis, structure, and reactions of group I and II alanates, amides, and borohydrides in “Complex Hydrides for Hydrogen Storage”. These materials are referred to as complex hydrides and represent promising materials for on-board hydrogen storage for vehicular applications. The significant progress made toward understanding the thermodynamics and improving the kinetics of dehydrogenation and rehydrogenation is examined along with the effects of dopants or catalysts as well as the remaining scientific challenges.

In their article “Hydrogen Storage in Molecular Clathrates”, Struzhkin, Militzer, Mao, Mao, and Hemley review the experimental and theoretical aspects of hydrogen clathrates, where hydrogen is stored in a supramolecular assembly. This is a fascinating recent discovery that could have significant future energy applications. Hydrogen is retained by weak van der Waals forces and interactions in these solid systems and can be released by changes in temperature or pressure. The structure and formation of hydrogen clathrates are discussed along with the experimental tools used to probe their structure and dynamics, including neutron scattering, Raman spectroscopy, and nuclear magnetic resonance. Recent theoretical developments including semiempirical and *ab initio* methods are also reviewed. Approaches based on supramolecular chemistry hold significant potential for new materials and processes for hydrogen storage.

Kubas provides a review of the fundamentals of hydrogen binding and reactivity in transition metal dihydrogen complexes, which were first discovered in the author’s laboratory. As described in his article “Fundamentals of H_2 Binding and Reactivity on Transition Metals Underlying Hydrogenase Function and H_2 Production and Storage”, over 500 complexes have now been found where dihydrogen is bound in a side-on σ complex to transition metal centers. These species may be relevant to a number of catalytic processes. The potential ramifications of dihydrogen complexes for hydrogen production, hydrogen storage, and metal binding of hydrogen in biological systems including hydrogenases are examined along with the experimental and theoretical tools to investigate these fascinating compounds.

In nature the process of hydrogen generation or utilization is performed by the enzyme hydrogenase. In their article “Occurrence, Classification, and Biological Function of Hydrogenases: An Overview”, Vignais and Billoud review the wide distribution of the different hydrogenases in the living world. The astonishing diversity of organisms using H_2 is described, and their classification is introduced. The recent work on the biosynthesis of [NiFe]- and [FeFe]-hydrogenases as well as that of [Fe−S] clusters is reviewed and their evolutionary relationship outlined. The article ends with the description of the different roles of hydrogenases in nature, touching upon interesting topics such as the formation of methane, the fixation of nitrogen, biohydrogen production, bioremediation, and pathological processes.

The review by Fontecilla-Camps, Volbeda, Cavazza, and Nicolet on “Structure/Function Relationships of [NiFe]- and [FeFe]-Hydrogenases” provides a structural basis for understanding hydrogenase function. The authors first describe the isolation and crystallization of the enzyme and its structural analysis *via* X-ray crystallography. Structures with high resolution are now available for several of the catalytic [NiFe]- and [FeFe]-hydrogenases, whereas information is still lacking for other interesting classes, such as the oxygen-insensitive hydrogenases (*e.g.*, from *Ralstonia eutropha*), the hydrogenases from photosynthetic bacteria, and those from green algae (*e.g.*, *Chlamydomonas*). The authors outline the primary importance of structural knowledge for understanding the function of the enzymes. In addition to the geometrical arrangement of the catalytic site, the putative hydrogen channels through the protein, the electron transport chain (via iron−sulfur centers), and the pathway for the protons are described. Additional sections are devoted to the maturation of the enzymes, to the problem of oxygen sensitivity, and to substrate binding and the catalytic process. An interesting additional aspect is the comparison of the hydrogenases with other proteins and their possible evolutionary relationship.

Although the X-ray structural analysis is a very useful tool, the information provided by this method is not sufficient to fully understand the details of hydrogenase function. Moreover, it is often difficult to obtain structures of key intermediates, which are frequently quite short-lived. In their article, “Activation and Inactivation of Hydrogenase Function and the Catalytic Cycle: Spectroelectrochemical Studies”, De Lacey, Fernández, Rousset, and Cammack describe the important additional information that is obtained from spectroscopic methods such as electron paramagnetic resonance (EPR), X-ray absorption (XAS), Mossbauer, and infrared methods (FTIR), performed under control of redox potential and catalytic activity. Such methods deliver supplementary information and sometimes new insight, particularly about the electronic structure of these enzymes in the various stages of the catalytic cycle. Furthermore, the activation and inactivation/inhibition of the enzyme can be investigated by these techniques. The authors also describe a variety of mutants that were designed to change and thereby probe the active site as well as the hydrogen access channel and the electron and proton transfer chains.

A particular problem in the investigation of the enzyme hydrogenase is that X-ray crystallography is practically blind for the substrate of this enzyme, *i.e.*, for hydrogen atoms, especially when they are bound to or near metal centers. Hydrogen can, however, be easily detected by magnetic resonance methods, which are the most sensitive to hydrogen and thus deliver a wealth of information on the geometric and electronic structure of the active site in hydrogenases. Such approaches are described in the article by Lubitz, Reijerse, and van Gastel, “[NiFe] and [FeFe] Hydrogenases Studied by Advanced Magnetic Resonance Techniques”, who review the use of modern EPR and related techniques such as pulse electron−nuclear double resonance (ENDOR) and two-dimensional electron spin echo envelope modulation (2D-ESEEM) to study the paramagnetic states of various hydrogenases with high spectral and time resolution, preferably in single crystals. These methods also provide important information on the electronic structure, *e.g.*, the metal oxidation states, the orbital occupations, and the spin density distribution. The article highlights the comparison of spectroscopic results with theoretical calculations performed on geometry optimized structures. This approach provides pertinent information on the hydrogenase intermediate states, from which the reaction mechanism can be obtained.

In their article "Investigating and Exploiting the Electrocatalytic Properties of Hydrogenases", Vincent, Parkin, and Armstrong describe the application of electrochemical techniques to hydrogenase reactivity and function, particularly protein film voltammetry (PFV), in which the hydrogenase is attached to a carbon electrode. This method records the current as a result of electron transfer and catalytic activity as a function of the electrode potential. The authors demonstrate that PFV allows for extensive exploration of hydrogenase properties, complementing other structural and spectroscopic investigations. The electrochemical potential is an important variable—both *in vitro* and *in vivo*—for tuning the catalytic activity, and it also controls the sensitivity of the enzyme to inhibition and destructive agents such as molecular oxygen. The authors also call out some potential applications. They show that hydrogenase-coated electrodes are stable and highly active in hydrogen oxidation and could perhaps even be used in fuel cells.

Theoretical attempts to elucidate details of H—H bond cleavage and formation by the enzyme hydrogenase are investigated in the review by Siegbahn, Tye, and Hall, "Computational Studies of [NiFe] and [FeFe] Hydrogenase". The authors describe the experimental findings and the different theoretical approaches used by various authors to elucidate the catalytic mechanisms of the [NiFe]- and the [FeFe]-hydrogenases. Such theoretical work can provide important insight into the details of the reaction sequences and help to answer some of the critical questions in hydrogenase research. Theory is also important to assist in the interpretation of spectroscopic data.

Articles in this thematic issue illustrate how scientists from different fields have contributed to the present understanding of the structure, function, and dynamics of the different hydrogenases. Understanding how natural systems function can provide important insight for the design of new catalytic processes including artificial bioinspired catalysts, *e.g.*, for efficient hydrogen generation, preferably from water and sunlight. Other articles clearly demonstrate that significant insights are also being developed that will impact how we eventually produce, store, and use hydrogen. The current picture is far from complete, but recent years have seen significant progress, largely due to advances in synthetic methods and analytical tools, as well as the broader application of theory. We hope that the excellent articles on various aspects of hydrogen presented in this thematic issue will inspire many scientists, in particular the younger generation, to become involved with this important topic and energy-related fields in general. As Esswein and Nocera state at the end of their review article in this issue, "the chemical community as a whole can contribute to the scientific toolbox necessary for society to use hydrogen directly or indirectly as the primary energy carrier of the future".

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