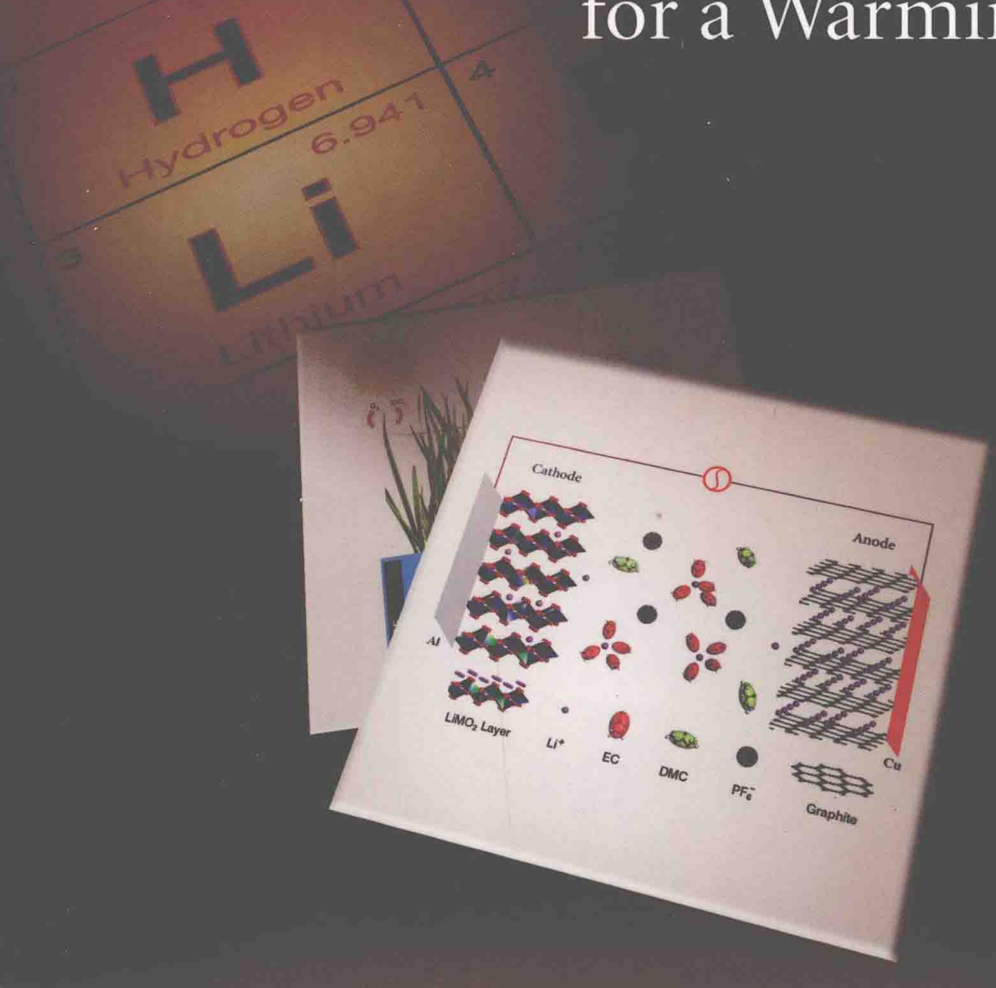
Editor
Robert H. Crabtree

Energy Production and Storage

Inorganic Chemical Strategies for a Warming World



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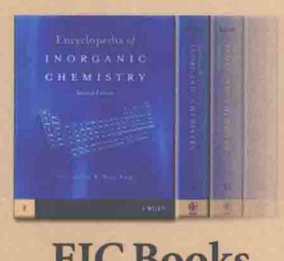

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ENERGY PRODUCTION AND STORAGE

Inorganic Chemical Strategies for a Warming World

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Encyclopedia of Inorganic Chemistry

In 1994 John Wiley & Sons published the *Encyclopedia of Inorganic Chemistry* (EIC). This 8-volume work was well received by the community, and has become a standard publication in all libraries serving the inorganic, coordination chemistry, organometallic and bioinorganic communities. The 10-volume Second Edition of the *Encyclopedia* was published in print in 2005, and online in 2006, on the major reference platform Wiley Online Library. The online edition is regularly updated and expanded. For more information see:

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ENERGY PRODUCTION AND STORAGE

Inorganic Chemical Strategies for a Warming World

Editor

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WILEY

This edition first published 2010

Registered office

John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

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Library of Congress Cataloging-in-Publication Data

Energy production and storage : inorganic chemical strategies for a warming world / editor, Robert H. Crabtree.
p. cm.
Includes bibliographical references and index.
ISBN 978-0-470-74986-9 (cloth: alk. paper)
1. Hydrogen as fuel--Research. 2. Water resources development. 3. Renewable energy sources. 4. Environmental chemistry. 5. Carbon sequestration. I. Crabtree, Robert H., 1948-
TP359.H8E54 2010
621.042--dc22

2010025736

A catalogue record for this book is available from the British Library.

ISBN-13: 978-0-470-74986-9

Set in 9½ / 11½ pt TimesNewRomanPS by Laserwords (Private) Limited, Chennai, India.
Printed and bound in Singapore by Markono Print Media Pte Ltd.

Encyclopedia of Inorganic Chemistry

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Series Preface

The success of the *Encyclopedia of Inorganic Chemistry* (EIC) has been very gratifying to the editors. We felt, however, that not everyone would necessarily need access to the full ten volumes of EIC. Some readers might prefer to have more concise thematic volumes targeted to their specific area of interest. This idea encouraged us to produce a series of EIC Books, focusing on topics of current interest. These will continue to appear on a regular basis and will feature the leading scholars in their fields. Like the Encyclopedia, we hope that EIC Books will give both the starting research student and the confirmed research worker a critical distillation of the leading concepts and provide a structured entry into the fields covered.

Computer literature searches have become so easy that one could be led into thinking that the problem of efficient access to chemical knowledge is now solved. In fact, these searches often produce such a vast mass of material that the reader is overwhelmed. As Henry Kissinger has remarked, the end result is often a shrinking of one's perspective. From studying the volumes that comprise the EIC Books series, we hope that readers will find an expanding perspective to furnish ideas for research, and a solid, up-to-date digest of current knowledge to provide a basis for instructors and lecturers.

I take this opportunity of thanking Bruce King, who pioneered the *Encyclopedia of Inorganic Chemistry*, my fellow editors, as well as the Wiley personnel, and, most particularly, the authors of the articles for the tremendous effort required to produce such a series on time. I hope that EIC Books will allow readers to benefit in a more timely way from the insight of the authors and thus contribute to the advance of the field as a whole.

Robert H. Crabtree
Yale University, New Haven, CT, USA

January 2009

Volume Preface

Energy production and storage are central problems for our time and are likely to attract intense public attention during many future decades. One factor will be the gradual decline in world petroleum production, as we pass the moment of peak production at some point in the next few years. The petroleum age is not over, of course, but the era of *cheap* petroleum does seem to be over. Oil wealth can also be associated with political instability, with unpredictable results on supply. A new factor—the economic rise of Asia and her vast population—can only aggravate the situation. Coal, the fossil fuel with the greatest reserves and with the broadest geographical distribution, may be able to fill any future energy supply gap but only at the cost of environmental damage at the mine and more intense CO_2 emissions—coal having the highest CO_2 output per unit of energy produced. Carbon capture and storage is under intense study but its practicality as a low-carbon-footprint means of using coal is still under discussion. Natural gas has been widely acclaimed as the best of the fossil fuels, having the lowest CO_2 output per unit of energy produced. Hopes exist that abundant and widely distributed shale gas, previously considered uneconomic, may become viable with rising energy prices and new production methods.

A key factor that has intensified the growing unease over our current energy production system is the threat of climate change. David King, the UK Government's Chief Science Advisor from 2000 to 2007, has even called climate change "the single biggest challenge our civilization has ever had to face." Nuclear energy is a potential solution but the problem of waste management has not yet been satisfactorily solved.

This volume is particularly concerned with alternative energy production and storage. Abundant energy is, in principle, available from the sun to run the earth in a sustainable way. Solar energy can be directly harnessed by agricultural and photovoltaic means but the sheer scale of the energy demand poses severe challenges. For example, any major competition between biomass production and food production would simply transfer scarcity from energy to food. Indirect use of solar energy in the form of wind is also promising, especially for those regions not blessed with abundant sunlight. Other modes such as tidal and wave energy may well be niche players.

These are problems in which chemistry can play a decisive role. The present volume covers some promising modes of alternative energy production and storage that minimize the atmospheric burden of fossil-derived CO_2. No one production or storage mode is likely to dominate, at least at first, and numerous possibilities need to be explored to compare their technical feasibility and economics. This provides the context for a broad exploration of novel ideas that we are likely to see in future years as the field expands.

Water splitting is a central problem in alternative energy work. Only water is a sufficiently cheap and abundant electron source for global exploitation, as Jules Verne foresaw in his 1874 novel, *The Mysterious Island*, "water will be the coal of the future." Of course, both energy input and suitable catalysts are needed to split water into oxygen and either hydrogen or electrons and protons. In this context, Brudvig and coauthors discuss energy conversion in photosynthesis, Llobet and coauthors cover molecular water splitting catalysts, Brewer and coauthors consider photocatalytic hydrogen production from water and T-Raissi covers thermochemical water splitting. Johannson and coauthors discuss recent progress in the Swedish Consortium for Artificial Photosynthesis. Batista discusses the progress made in computational modeling of energy-related processes including photosynthesis.

Several articles concentrate on hydrogen, notably a key contribution on the hydrogen economy by Edwards and coauthors and on hydrogen production from renewables by Fierro and coauthors.

A number of important chemical conversions are covered, for example reduction of CO_2 to useful fuels either electrochemically or photochemically, as well as conversion of methane to methanol by Periana and coauthors.

Dye-sensitized solar cells for the direct conversion of solar to electrical energy is reviewed by Mendes and coauthors. Related to this problem, Meyer and coauthors discuss photoinitiated electron transfer in such cells.

A number of articles relate to fuel cells. Devanathan discusses the key problem of devising efficient proton exchange membranes, Brett covers intermediate temperature solid oxide fuel cells, Lee considers direct ethanol fuel cells, Oyaizu considers molecular catalysis for fuel cells, and Barrière covers the use of enzymes and microbes in fuel cells.

Batteries are also considered. Lucht and coauthors discuss Li ion batteries, Grey and coauthors cover L-6 MAS NMR studies on battery materials, and Zhao reviews the

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PART 1
Energy Production

H_2 Production from Renewables

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1 INTRODUCTION

Energy and environmental concerns are among the biggest challenges that the world is facing today, in particular, energy sustainability and carbon emission from the fossil fuels. Hydrogen is considered as one of the few long-term sustainable clean energy carriers, emitting only water vapor as a by-product during its oxidation or combustion. Although hydrogen can be used as a fuel in internal combustion engines (ICEs), the conversion of the chemical energy stored in the H–H bond into electricity in fuel cells is more attractive because of its higher efficiency.[1]

Production of H_2 by the currently available technologies consumes greater amounts of natural gas, which in turn emits more greenhouse gas (GHG). However, in spite of using nonrenewable fossil fuel feedstock, the increase in GHG emissions can be reduced through CO_2 sequestration at the production sites. Production of H_2 from renewable sources derived from agricultural or other waste streams offers the possibility to contribute to the production capacity with lower or no net GHG emissions, without carbon sequestration technologies, increasing the flexibility and improving the economics of distributed and semicentralized reforming.

At present, steam reforming of hydrocarbons, i.e., natural gas, is the most commonly used and generally the most economical method for hydrogen production.[2–5] The use of natural gas, whose major component is methane, fails to provide a solution to deal with the large amount of carbon dioxide emissions (ca 7 kg CO_2/kg H_2) during the reforming processes. In addition, the use of fossil fuels for secondary energy production is nonsustainable. Not only does fossil fuel burning contribute to the GHG pool but the eventual depletion of the world's fossil fuel reserves also threatens sustainable development.[6,7] However, hydrogen production can be environmentally friendly only if the resource used to extract hydrogen is renewable. Thus, biomass, a product of photosynthesis, is an attractive alternative to fossil feedstocks as it can be considered as a renewable H_2 precursor. CO_2-neutral hydrogen can be produced by the conversion of biomass via gasification,[8] pyrolysis of bio-oils,[9] steam reforming of biomass-derived higher alkanes and alcohols,[2,5,10] and aqueous phase reforming (APR) of oxygenated hydrocarbons.[11] Biomass-derived hydrogen can be classified as carbon neutral because the CO_2 released during hydrogen production is further consumed by biomass generation (neglecting the CO_2 produced from the fossil

Energy Production and Storage. Edited by Robert H. Crabtree. © 2010 John Wiley & Sons, Ltd. ISBN 978-0-470-74986-9

fuel energy required for operating the hydrogen production unit).[12]

Among the methods for H_2 generation outside the C-cycle, hydrogen production using solar energy also attracts great attention because of the potential to use the abundance of this energy (the maximum direct insolation frequently reaches ca $700\,W\,m^{-2}$ in the sunbelt regions) and water. Thermodynamically, the overall water-splitting reaction is an uphill reaction, with a highly positive change in Gibbs free energy ($\Delta G^0 = +237.2\,kJ\,mol^{-1}$):

$$H_2O(l) \longrightarrow H_2(g) + \frac{1}{2}O_2(g) \quad (\Delta G^0 = +237.2\ kJ\ mol^{-1}) \quad (1)$$

Solar energy can be used to produce hydrogen in the form of heat (thermochemical), light (photoelectrochemical or photocatalytic), or electricity (electrolysis). Among these, thermochemical, photoelectrochemical, and photocatalytic are the most efficient solar paths to hydrogen since they do not have the inefficiencies associated with the conversion of solar energy to electricity followed by electrolysis.

In this article, we review the recent developments in the conversion involved in hydrogen production from less costly and abundant biomass without net carbon emissions. In addition, this article includes advances in the fully renewable conversion of solar energy into hydrogen via the water-splitting process assisted by thermochemical, photolectrochemical, and photocatalytic processes. Attention is particularly given to the new materials and strategies reported in the literature over the past years for developing efficient metal oxide redox cycles for a two-step thermochemical water splitting, efficient photoelectrocatalysts under visible light photocatalysts for hydrogen evolution via photoelectrochemical water splitting, and efficient photocatalysts under visible light for the photochemical water splitting.

2 HYDROGEN PRODUCTION FROM BIOMASS

Figure 1 illustrates the different routes that can be adopted to produce hydrogen from biomass, including gasification to produce syngas, pyrolysis to produce bio-oils, and hydrolysis of cellulose to produce sugar monomers.[13] syngas can be converted to hydrogen by water gas shift (WGS) reaction, though any remaining CO must be removed from the gas stream. Pyrolysis bio-oil can be converted to liquid fuel, but the processes are complex and the rate of conversion is low. Hydrogen can be produced from the bio-oil by autothermal reforming with high conversion efficiency, especially with the use of catalytic membrane reactors. APR can be used to convert sugars and sugar alcohols, such as sorbitol, to produce hydrogen. In addition to these, there are other biological (enzymatic and bacterial) routes to produce hydrogen, but the scope of this article is restricted only to the heterogeneous catalytic routes.

2.1 Gasification

Biomass gasification is achieved at temperatures above 1000 K in the presence of oxygen/air and/or steam. A combination of pyrolysis, partial oxidation, and/or steam-reforming reactions of gaseous alkanes and char takes place under these conditions. The presence of oxygen or air in the gasification equipment promotes partial oxidation over pyrolysis reactions. Although gaseous products (H_2 and CO_x) are mainly obtained, the fast pyrolysis reactions can also produce bio-oils, tar (aromatic hydrocarbons), and charcoal. Several parameters such as heating rate, temperature, and residence time can be optimized to maximize the efficiency of gasification with minimum tar formation. Thermal cracking of the tar is possible at temperatures above 1300 K[14] and by using catalytic additives such as dolomite, olivine, and char,[15] with 100% removal of tar by using dolomite as the gasifying agent.[16] Moreover, dolomite and CeO_2/SiO_2-supported Ni, Pt, Pd, Ru, and alkaline metal oxides can be used to catalyze the gasification process to reduce tar formation and improve the product gas purity and conversion efficiency.[17] Although $Rh/CeO_2/SiO_2$ has been reported to be the most effective catalyst to reduce tar formation, Ni-based catalysts are also highly active for tar destruction. Since Ni-based catalysts are industrially used for steam reforming of methane and naphtha,[5]

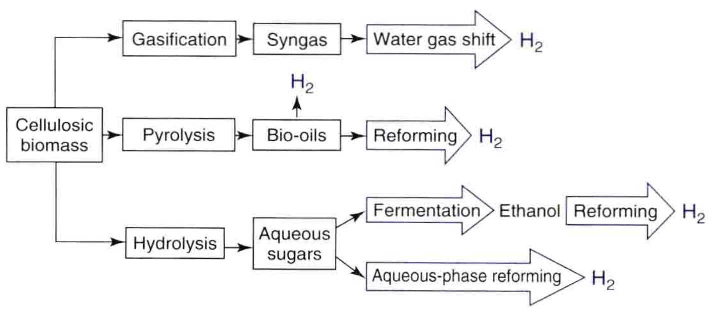

Figure 1 Routes to the production of hydrogen from biomass