Solar Hydrogen Generation

# Solar Hydrogen Generation

# Toward a Renewable Energy Future

Edited by

Krishnan Rajeshwar University of Texas at Arlington, TX, USA

Robert McConnell Amonix, Inc., Torrance, CA, USA

Stuart Licht University of Massachusetts, Boston, USA



*Editors* Krishnan Rajeshwar Department of Chemistry & Biochemistry University of Texas, Arlington Arlington TX 76019-0065 USA rajeshwar@uta.edu

Robert McConnell Amonix, Inc. 3425 Fujita St. Torrance, CA 90505 bob@amonix.com

Stuart Licht Chemistry Division National Science Foundation 4201 Wilson Blvd. Arlington, VA 022230 USA slicht@nsf.gov

Department of Chemistry University of Massachusetts, Boston 100 Morrissey Blvd. Boston MA 02135 USA stuart.licht@umb.edu

ISBN: 978-0-387-72809-4

e-ISBN: 978-0-387-72810-0

Library of Congress Control Number: 2007943478

© 2008 Springer Science+Business Media, LLC

All rights reserved. This work may not be translated or copied in whole or in part without the written permission of the publisher (Springer Science+Business Media, LLC, 233 Spring Street, New York, NY 10013, USA), except for brief excerpts in connection with reviews or scholarly analysis. Use in connection with any form of information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed is forbidden.

The use in this publication of trade names, trademarks, service marks, and similar terms, even if they are not identified as such, is not to be taken as an expression of opinion as to whether or not they are subject to proprietary rights.

Printed on acid-free paper

987654321

springer.com

### Dedication

#### Krishnan Rajeshwar

To the three girls in my life, Rohini, Reena, and Rebecca: I could not have done this without your love and support

#### **Robert McConnell**

To my wife Suzie Star whose love and support made this possible. To my children and especially my grandson Tharyn. My hope for them is to live in a cleaner world powered by renewable energy and hydrogen.

#### Stuart Licht

To my children: Reeva, Gadi, Ariel, Jacob and Dov; I hope to open a path to a sustainable energy future for them. To my wife Bregt, this is here because you are here.

## Preface

This book examines ways to generate hydrogen from sunlight and water. It largely arose out of a desire to bring all the disparate ways to accomplish this goal within the confines of a single edited volume. Thus we are aware of many books and reports discussing the pros and cons of a hydrogen economy but none, that we are aware of, that focus on the science and technology of generating hydrogen from sunlight and water. While renewable hydrogen currently remains an elusive goal, at least from a cost perspective, the *scientific* principles behind its generation are well understood. Thus over and above reviewing this substantial fundamental database, part of the incentive for creating this book was to hopefully inspire future generations of scientists and engineers to respond to the grand challenge of translating the impressive laboratory advances and prototype demonstrations to a practical renewable energy economy. Much of this daunting hurdle has to do with optimizing the efficiency and hence the cost-effectiveness of hydrogen producing solar energy systems.

History certainly is on our side in meeting this challenge. Many early civilizations used the sun, water, and the wind to meet basic needs. Even geothermal heat was used by North American Indians some 10,000 years ago for cooking. The ancient Greeks used hydro power to grind flour and the Persians used windmills to pump water in the first millennium. The human race is very good at solving technological problems and we can certainly wean ourselves from fossil fuels if we collectively put our minds to it. But cost is certainly going to be a driver and no amount of civic sense is going to render the hydrogen economy practically realizable if a gallon of gasoline continues to be substantially cheaper than a kilogram of hydrogen. Unfortunately however we can only give short shrift to the issue of economics in this book because of the rapidly shifting landscape of assumptions that an evolving technology brings with it. Nonetheless, the concluding chapter of this book examines investments, levelized hydrogen prices, and fuel cycle greenhouse gas emissions of a centralized electrolytic hydrogen production and distribution system powered by photovoltaic electricity.

Another important and related topic, not specifically addressed in this book, concerns the issue of how to store hydrogen, especially in a mobile transportation application. We felt that this topic was specialized and wide ranging enough to warrant a separate volume to be created by scientists and engineers far more qualified and knowledgeable than us. While fuel cells are briefly introduced in Chapter 1, how hydrogen is to be utilized to generate power is again left to many other excellent treatises in the literature; some of these are cited in what follows.

Every effort was made to remove redundancy and add homogeneity to the material in this multi-author volume. Indeed, the more authoritative level of discussion afforded by having specialists write each chapter will have hopefully overridden any "rough edges" that remain from chapter to chapter. Undoubtedly, many flaws remain for which we as editors are wholly responsible; we would welcome feedback on these.

A project of this magnitude could not have been completed without the collective contributions of many people, some of whom we wish to acknowledge at this juncture. First, Ken Howell deserves special thanks for his many useful suggestions. His patience as this book production went through countless delays is also much appreciated. Don Gwinner, Al Hicks and their production team at NREL managed to create quality illustrations from the drawings and graphs (many in primitive form) that were furnished to them. Maria Gamboa is thanked for very capably doing the pre-print lay-out of the various manuscripts. Finally we offer simple thanks to our families for their love and support and for putting up with the many weekends away spent in putting this volume together.

Krishnan Rajeshwar Arlington, Texas

Robert McConnell Torrance, CA

Stuart Licht Washington, DC

# Contents

Pr	Prefacevii			
1.	Rer	newable Energy and the Hydrogen Economy	1	
	Krishnan Rajeshwar, Robert McConnell, Kevin Harrison,			
		and Stuart Licht		
	1	Renewable Energy and the Terawatt Challenge	1	
	2	Hydrogen as a Fuel of the Future		
	3	Solar Energy and the Hydrogen Economy		
	4	Water Splitting and Photosynthesis		
	5	Completing the Loop: Fuel Cells		
	6	Concluding Remarks		
		References		
2.	The	e Solar Resource	19	
	Daryl R. Myers			
	1	Introduction: Basic Properties of the Sun	19	
	2	The Spectral Distribution of the Sun as a Radiation Source		
	3	The Earth's Atmosphere as a Filter		
	4	Utilization of Solar Spectral Regions: Spectral Response of		
		Materials	25	
	5	Reference Spectral Distributions	32	
	6	Summary		
		References		
3.	Ele	Electrolysis of Water41		
	Kev	in Harrison and Johanna Ivy Levene		
	1	Introduction		
	2	Electrolysis of Water	43	

		2.1 Alkaline	44			
		2.2 Proton Exchange Membrane	45			
	3	Fundamentals of Water Electrolysis	50			
		3.1 First Principles	50			
		3.2 Overpotentials				
	4	Commercial Electrolyzer Technologies	54			
	5	Electrolysis System	55			
		5.1 Energy Efficiency	56			
		5.2 Electricity Costs				
	6	Opportunities for Renewable Energy				
	7	Conclusions				
		References	61			
4.		olar Concentrator Pathway to Low-Cost Electrolytic Hydrogen ert McConnell	65			
	1	Direct Conversion of Concentrated Sunlight to Electricity	65			
	2	The CPV Market				
	3	Higher and Higher Conversion Efficiencies	69			
	4	CPV Reliability				
	5	Following in Wind Energy's Footsteps	73			
	6	Low-Cost Hydrogen from Hybrid CPV Systems				
	7	Describing the Hybrid CPV System				
	8	Discussion				
	9	Hydrogen Vision Using Hybrid Solar Concentrators	82			
	10	Conclusions				
		Acknowledgements				
		References	84			
5.		rmochemical and Thermal/Photo Hybrid Solar Water Splitting rt Licht	87			
	1	Introduction to Solar Thermal Formation of Hydrogen	87			
		1.1 Comparison of Solar Electrochemical, Thermal & Hybrid				
		Water Splitting	87			
	2	Direct Solar Thermal Water Splitting to Generate Hydrogen Fuel				
		2.1 Development of Direct Solar Thermal Hydrogen				
		2.2 Theory of Direct Solar Thermal Hydrogen Generation				
		2.3 Direct Solar Thermal Hydrogen Processes				
	3	Indirect (Multi-step) Solar Thermal Water Splitting to Generate				
		Hydrogen Fuel	94			
		3.1 Historical Development of Multi-Step Thermal Processes	0.4			
		<ul><li>for Water Electrolysis</li></ul>	94			
			07			
		Hydrogen Processes	90			
		3.3 High-Temperature, Indirect-Solar Thermal Hydrogen	04			
		Processes	90			

	4	Hybrid Solar Thermal/Electrochemical/Photo (STEP) Water Splitting		99				
		4.1	Historical Development of Hybrid Thermal Processes					
		4.2	Theory of Hybrid Solar Hydrogen Generation					
		4.3	Elevated Temperature Solar Hydrogen Processes and					
			Components	111				
	5	Future	e Outlook and Concluding Remarks					
	5		ences					
		Kelen		110				
6.			Approaches to Photochemical Splitting of Water	cal Splitting of Water123				
	Free		1. MacDonnell					
	1							
	2		mental Principles					
	3		e's Photosynthetic Machinery					
	4		n of Artificial Photosystems					
	5	The Id	leal Sensitizer: Does Rubpy Come Close?	133				
		5.1	Stability	133				
		5.2	Photophysics and Photochemistry	136				
	6	Supra	molecular Assemblies: Dyads, Triads and Beyond	138				
		6.1	Energy Transfer Quenching: Antenna Complexes	138				
		6.2	Bichromophores: Increasing Excited-State Lifetimes	140				
		6.3	Reductive and Oxidative Quenching: Dyads and Triads					
			with Donors and Acceptors	142				
		6.4	Single versus Multi-Electron Processes	145				
	7.	OER a	and HER Co-Catalysts					
		7.1	Mimicking the Oxygen Evolving Center: Water Oxidation					
			Catalysts	150				
		7.2	The Hydrogen Evolving Reaction (HER): Hydrogen					
			Evolution Catalysts	153				
	8. Future Outlook and Concluding Remarks							
			owledgements					
			ences					
7.	Hyd	lrogen	Generation from Irradiated Semiconductor-Liquid					
			*	167				
			ajeshwar					
	1		uction and Scope	167				
			of Approaches					
	3	More on Nomenclature and the Water Splitting Reaction						
	Requirements							
	4		ency of Photoelectrolysis					
	5		etical Aspects					
	6 Oxide Semiconductors							
	U	6.1	Titanium Dioxide: Early Work	183				
		0.1	Finitum Dioxide. Darry Work	105				

	6.2	Studies on the Mechanistic Aspects of Processes at the	
		TiO <sub>2</sub> -Solution Interface	186
	6.3	Visible Light Sensitization of TiO2	186
	6.4	Recent Work on TiO <sub>2</sub> on Photosplitting of Water or on the	
		Oxygen Evolution Reaction	187
	6.5	Other Binary Oxides	190
	6.6	Perovskite Titanates and Related Oxides	192
	6.7	Tantalates and Niobates	
	6.8	Miscellaneous Multinary Oxides	198
7	Nitrid	les, Oxynitrides and Oxysulfides	200
8	Metal	Chalcogenide Semiconductors	
	8.1	Cadmium Sulfide	
	8.2	Other Metal Chalcogenides	204
9	Group	p III-V Compound Semiconductors	205
10	Germ	anium and Silicon	206
11	Silver	Halides	208
12	Semio	conductor Alloys and Mixed Oxides	208
	12.1	Semiconductor Composites	208
13	Photo	chemical Diodes and Twin-Photosystem Configurations for	
	Water	r Splitting	210
14	Other	Miscellaneous Approaches and Hydrogen Generation from	
	Media	a Other than Water	211
15	Concl	luding Remarks	213
	Ackn	owledgments	213
		ences	

8.	Pho	tobiolog	gical Methods of Renewable Hydrogen Production	229
	Maria L. Ghirardi, Pin Ching Maness, and Michael Seibert			
	1 Introduction		iction	229
	2	Green Algae		230
		2.1	Mechanism of Hydrogen Production	
		2.2	Hydrogenase-Catalyzed H <sub>2</sub> Production	
		2.3	[FeFe]-hydrogenases	234
	3	Cyanobacteria		
		3.1	Mechanisms of Hydrogen Production	
		3.2	Hydrogenase-Catalyzed H <sub>2</sub> Production	
		3.3	[NiFe]-Hydrogenases	
		3.4	Nitrogenase-Catalyzed H2 Production	
		3.5	Nitrogenases	
	4.	Other Systems		
		4.1	Non-Oxygenic Purple, Non-Sulfur Photosynthetic Bacteria	242
		4.2	Mixed Light/Dark Systems	243
		4.3	Bio-Inspired Systems	
	5	Scientific and Technical Issues		
		5.1	General	
		5.2	Oxygen Sensitivity of [FeFe]-Hydrogenases	

		5.3	Oxygen Sensitivity of [NiFe]-Hydrogenases	248		
		5.4	Competition between Different Pathways for			
			Photosynthetic Reductants	249		
		5.5	Down-Regulation of Electron Transport Rates			
		5.6	Low-Light Saturation Properties of Photosynthetic			
			Organisms	251		
		5.7	Photobioreactor and System Costs			
		5.8	Genomics Approaches.			
	6	Future	Directions			
	U		wledgments			
			nces			
		itererer				
9.	Cen	tralized	Production of Hydrogen using a Coupled Water			
			r-Solar Photovoltaic System	273		
			n and Ken Zweibel			
	1	Introdu	lection	273		
	2	Descrip	otion of a PV Electrolytic H <sub>2</sub> Production and Distribution			
			· · · · · · · · · · · · · · · · · · ·	274		
	3		Investment and Levelized Price Estimates			
	4		vity Analysis: H <sub>2</sub> Production and PV Electricity Prices			
	5	Economic Analysis of Second Generation (Year 31–Year 60) H <sub>2</sub>				
	-		18	289		
	6		cle Energy and GHG Emissions Analyses			
		6.1	Life Cycle Analysis Methods			
		6.2	Life Cycle Energy and GHG Emissions Analyses Results			
	7	System	Energy Flow/Mass/Balance Analysis			
	8					
	-		is	298		
			dices			
		1	Energy Units and CO <sub>2</sub> Equivalent Emissions Estimates			
		2	Levelized Price Estimates Derived by Net Present Value			
			Cash Flow Analysis			
		3	Adiabatic Compression Formula			
		4	Deviations from DOE H2A Assumptions			
		5	Summary of Reviewer Comments with Responses			
			nces			
		1.010101				
In	dex .			315		

# Contributors

Maria L. Ghiradi, National Renewable Energy Laboratory 1617 Cole Blvd., Golden, CO 80401 marie\_ghiradi@nrel.gov

Kevin Harrison National Renewable Energy Laboratory NREL MS3911 1617 Cole Blvd., Golden, CO 80401 Ph: 303-384-7091, F:303-384-7055, Kevin\_Harrison@nrel.gov

Johanna Ivy Levene National Renewable Energy Laboratory NREL MS3911 1617 Cole Blvd., Golden, CO 80401 johanna\_levene@nrel.gov

Stuart Licht Chemistry Division National Science Foundation 4201 Wilson Blvd., Arlington, VA 022230 Ph: 703-292-4952, slicht@nsf.gov

Chemistry Department 100 Morrissey Boulevard University of Massachusetts, Boston, MA 02135-3395 Ph: 617-287-6156, stuart.licht@umb.edu xvi Contributors

Frederick M. MacDonnell

Department of Chemistry and Biochemistry The University of Texas at Arlington, Arlington, TX 76019-0065 Ph: 817-272-2972, F:817-272-3808, macdonn@uta.edu

Pin Ching Maness National Renewable Energy Laboratory 1617 Cole Blvd., Golden, CO 80401 pinching\_maness@nrel.gov

James Mason Hydrogen Research Institute 52 Columbia St., Farmingdale, NY 11735 Ph: 516-694-0759, E: hydrogenresearch@verizon.net

Robert McConnell Amonix, Inc. 3425 Fujita St., Torrance, CA 90505 Ph: 310-325-8091, F: 310-325-0771, E: bob@amonix.com

Daryl Myers Electric System Center NREL MS3411 1617 Cole Blvd., Golden, CO 80401 Ph: 303-384-6768, F:303-384-6391, E: daryl\_myers@nrel.gov, W:http://www.nrel.gov/srrl

Krishnan Rajeshwar College of Science, Box 19065 The University of Texas at Arlington, Arlington, TX 76019 Ph: 817-272-3492, F:817-272-3511, E: rajeshwar@uta.edu,

Michael Seibert National Renewable Energy Laboratory 1617 Cole Blvd., Golden, CO 80401 Ph: 303-384-6279, F: 303-384-6150, mike\_seibert@nrel.gov

Ken Zweibel Primestar Solar Co., Longmont, CO ken.zweibel@primestarsolar.com

# **Biographical Sketches of Authors**

**Maria L. Ghirardi** is a Senior Scientist at NREL and a Research Associate Professor at the Colorado School of Mines. She has a B.S., an M.S. and a Ph.D degree in Comparative Biochemistry from the University of California at Berkeley and has extensive experience working with photosynthetic organisms. Her research at NREL involves photobiological H<sub>2</sub> production and covers metabolic, biochemical and genetic aspects of algal metabolism, generating over 60 articles and several patents.

**Kevin W. Harrison** is a Senior Engineer in the Electrical Systems Center at NREL. He received his Ph.D. at the University of North Dakota and leveraging management, automated equipment design and quality control experience, gained while working for Xerox Corporation, he joined NREL in 2006. At NREL he leads all aspects of the renewable hydrogen production task whose objective is to improve the efficiency and reduce the capital costs of a closely coupled wind to hydrogen demonstration project. Generally speaking his research interests are in reducing the environmental impact of the world's energy use by integrating and utilizing renewable energy for electricity and transportation fuels.

**Johanna Ivy Levene** is a Senior Chemical Applications Engineer at NREL. She specializes in the technical and economic analysis of electrolysis systems, and her current focus is the production of fuels from renewable resources. Prior to her work at NREL, Johanna has worked as a process control engineer, a database administrator, a systems administrator and a programmer. Results from her work have been published in Solar Today and Science.

**Stuart Licht** is a Program Director in the Chemistry Division of the National Science Foundation (NSF) and Professor of Chemistry at the University of Massachusetts, Boston. His research interests include solar and hydrogen energy, energy storage, unusual analytical methodologies, and fundamental physical chemistry. Prof. Licht received his doctorate in 1986 from the Weizmann Institute of Science, followed by a Postdoctoral Fellowship at MIT. In 1988 he became the first Carlson Professor of Chemistry at Clark University, and in 1995 a Gustella

Professor at the Technion Israel Institute of Science, in 2003 became Chair of the Department of Chemistry at the University of Massachusetts Boston, and in 2007 a Program Director at the NSF. He has contributed 270 peer reviewed papers and patents ranging from novel efficient solar semiconductor/electrochemical processes, to unusual batteries, to elucidation of complex equilibria and quantum electron correlation theory.

**F. M. MacDonnell** is Professor of Inorganic Chemistry at the University of Texas at Arlington (UTA). He received his PhD at Northwestern University in 1993. After a postdoctoral stint at the Chemistry Department of Harvard University, he joined the Chemistry and Biochemistry Department at UTA in 1995. His research interests are in the design of photocatalysts for light harvesting and energy conversion and has published over 100 articles in these areas.

**Pin Ching Maness** is a Senior Scientist at NREL. She received her Masters Degree in 1976 at Indiana State University, Terre Haute, IN. She worked as a Research Specialist at the University of California, Berkeley, CA from 1976 to 1980, before joining NREL in 1981. Her research interests are in studies of the physiology, biochemistry, and molecular biology of various biological  $H_2$ -production reactions in cyanobacteria, photosynthetic bacteria, and cellulolytic fermentative bacteria.

**James M. Mason** is Director of the Hydrogen Research Institute in Farmingdale, New York. He received his PhD at Cornell University in 1996. His research interests are the economic modelling of centralized hydrogen production and distribution systems using renewable energy sources.

**Robert D. McConnell** recently joined Amonix, Inc., a concentrator photovolatics (PV) company located in Torrance, CA as Director of Government Affairs and Contracts. He earned his PhD at Rutgers University in Solid State Physics following a Bachelor's degree in Physics at Reed College in Portland, Oregon. After a postdoctoral stint at the University of Montreal and employment at the research institute of the electric utility, Hydro Quebec, he joined NREL in 1978. He has authored numerous papers and edited or co-edited five books and chaired four international conferences on centrator PV. His technology interests include concentrator PV, future generation PV concepts, hydrogen, superconductivity, and wind energy. He has served as Chairman of the Energy Technology Division of the Electrochemical Society and is presently Convener of the international working group developing concentrator PV standards under the aegis of the International Electrotechnical Commission located in Geneva, Switzerland.

**Daryl R. Myers** is a Senior Scientist at NREI. In 1970 He received a Bachelor of Science in Applied Mathematics from the University of Colorado, Boulder, School of Engineering. Prior to joining NREL in 1978, he worked for four years at the Smithsonian Institution Radiation Biology Laboratory in Rockville Maryland, and is a Cold War veteran, serving as a Russian linguist in the United States Army from 1970 to 1974. He has over 32 years of experience in terrestrial broadband and spectral solar radiation physics, measurement instrumentation, metrology

(calibration), and modelling radiative transfer through the atmosphere. Daryl is active in International Lighting Commission (CIE) Division 2 on Physical Measurement of Light and Radiation, the American Society for Testing and Materials (ASTM) committees E44 on Solar, Geothermal, and Other Alternative Energy Sources and G03 on Weathering and Durability, and the Council for Optical Radiation Measurements (CORM).

**Krishnan Rajeshwar** is a Distinguished Professor in the Department of Chemistry and Biochemistry and Associate Dean in the College of Science at the University of Texas at Arlington. He is the author of over 450 refereed publications, several invited reviews, book chapters, a monograph, and has edited books, special issues of journals, and conference proceedings in the areas of materials chemistry, solar energy conversion, and environmental electrochemistry. Dr. Rajeshwar is the Editor of the Electrochemical Society Interface magazine and is on the Editorial Advisory Board of the Journal of Applied Electrochemistry. Dr. Rajeshwar has won many Society and University awards and is a Fellow of the Electrochemical Society.

Michael Seibert is a Fellow at the National Renewable Energy Laboratory in Golden, CO, USA. He received his Ph.D. in the Johnson Research Foundation at the University of Pennsylvania and then worked at GTE Laboratories before joining NREL (formerly the Solar Energy Research Institute) in 1977. His research has resulted in over 180 publications and several patents in the areas of materials development for electronic microcircuits, primary processes of bacterial and plant photosynthesis, cryopreservation and photomorphogenesis of plant tissue culture, water oxidation by photosystem II in plants and algae, microbial H, production, hydrogenase structure and function, genomics of Chlamydomonas, and computational approaches for improving H<sub>2</sub> metabolism in algae. He also holds a concurrent position as Research Professor at the Colorado School of Mines and is a Fellow of the AAAS.

**Ken Zweibel** is President of PrimeStar Solar, a CdTe PV company located in Colorado, USA. He graduated in Physics from the University of Chicago in 1970. He was employed for 27 years at SERI and then NREL in Golden, CO, where he worked on the development of CdTe, copper indium diselenide, and amorphous and thin film silicon. When he left in December 2006, he was manager of the Thin Film PV Partnership Program. He has published numerous papers and articles, and two books on PV, the most recent being, "Harnessing Solar Power: The PV Challenge." Besides the success of PrimeStar Solar, he is interested in solar policy and solutions to climate change and rising energy prices.