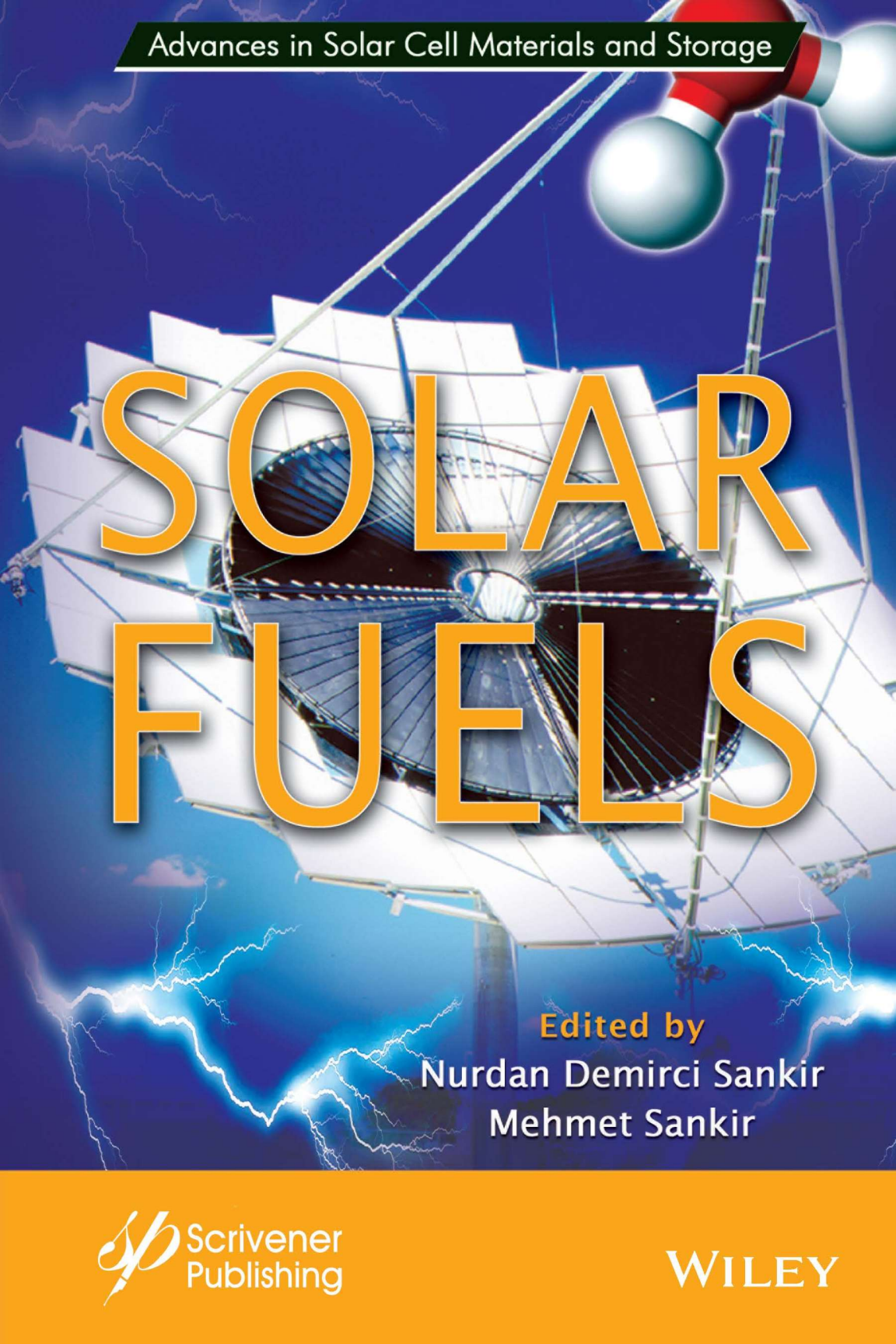


Advances in Solar Cell Materials and Storage

# SOLAR FUELS



Edited by

Nurdan Demirci Sankir

Mehmet Sankir

 Scrivener  
Publishing

WILEY



# Solar Fuels

**Scrivener Publishing**  
100 Cummings Center, Suite 541J  
Beverly, MA 01915-6106

## **Advances in Solar Cell Materials and Storage**

**Series Editor:** Nurdan Demirci Sankir and Mehmet Sankir

**Scope:** Because the use of solar energy as a primary source of energy will exponentially increase for the foreseeable future, this series on *Advances in Solar Cell Materials and Storage* will focus on new and novel solar cell materials and their application for storage. The scope of the series deals with the solution-based manufacturing methods, nanomaterials, organic solar cells, flexible solar cells, batteries and supercapacitors for solar energy storage, and solar cells for space.

*Publishers at Scrivener*

Martin Scrivener (martin@scrivenerpublishing.com)  
Phillip Carmical (pcarmical@scrivenerpublishing.com)

# Solar Fuels

Edited by

**Nurdan Demirci Sankir**

*Department of Materials Science and Engineering, TOBB University of Economics  
and Technology, Ankara, Turkey*

and

**Mehmet Sankir**

*Department of Materials Science and Engineering, TOBB University of Economics  
and Technology, Ankara, Turkey*



**WILEY**

This edition first published 2023 by John Wiley & Sons, Inc., 111 River Street, Hoboken, NJ 07030, USA and Scrivener Publishing LLC, 100 Cummings Center, Suite 541J, Beverly, MA 01915, USA

© 2023 Scrivener Publishing LLC

For more information about Scrivener publications please visit [www.scrivenerpublishing.com](http://www.scrivenerpublishing.com).

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, except as permitted by law. Advice on how to obtain permission to reuse material from this title is available at <http://www.wiley.com/go/permissions>.

#### **Wiley Global Headquarters**

111 River Street, Hoboken, NJ 07030, USA

For details of our global editorial offices, customer services, and more information about Wiley products visit us at [www.wiley.com](http://www.wiley.com).

#### **Limit of Liability/Disclaimer of Warranty**

While the publisher and authors have used their best efforts in preparing this work, they make no representations or warranties with respect to the accuracy or completeness of the contents of this work and specifically disclaim all warranties, including without limitation any implied warranties of merchantability or fitness for a particular purpose. No warranty may be created or extended by sales representatives, written sales materials, or promotional statements for this work. The fact that an organization, website, or product is referred to in this work as a citation and/or potential source of further information does not mean that the publisher and authors endorse the information or services the organization, website, or product may provide or recommendations it may make. This work is sold with the understanding that the publisher is not engaged in rendering professional services. The advice and strategies contained herein may not be suitable for your situation. You should consult with a specialist where appropriate. Neither the publisher nor authors shall be liable for any loss of profit or any other commercial damages, including but not limited to special, incidental, consequential, or other damages. Further, readers should be aware that websites listed in this work may have changed or disappeared between when this work was written and when it is read.

#### ***Library of Congress Cataloging-in-Publication Data***

ISBN 978-1-119-75057-4

Cover image: Pixabay.Com

Cover design by Russell Richardson

Set in size of 11pt and Minion Pro by Manila Typesetting Company, Makati, Philippines

Printed in the USA

10 9 8 7 6 5 4 3 2 1

# Contents

---

<b>Preface</b>	<b>xiii</b>
<b>Part I: Solar Thermochemical and Concentrated Solar Approaches</b>	<b>1</b>
<b>1 Materials Design Directions for Solar Thermochemical Water Splitting</b>	<b>3</b>
<i>Robert B. Wexler, Ellen B. Stechel and Emily A. Carter</i>	
1.1 Introduction	4
1.1.1 Hydrogen via Solar Thermolysis	7
1.1.2 Hydrogen via Solar Thermochemical Cycles	8
1.1.3 Thermodynamics	13
1.1.4 Economics	16
1.2 Theoretical Methods	17
1.2.1 Oxygen Vacancy Formation Energy	18
1.2.2 Standard Entropy of Oxygen Vacancy Formation	22
1.2.3 Stability	24
1.2.4 Structure	25
1.2.5 Kinetics	26
1.3 The State-of-the-Art Redox-Active Metal Oxide	26
1.4 Next-Generation Perovskite Redox-Active Materials	30
1.5 Materials Design Directions	33
1.5.1 Enthalpy Engineering	33
1.5.2 Entropy Engineering	37
1.5.3 Stability Engineering	41
1.6 Conclusions	42
Acknowledgments	42
Appendices	43
Appendix A. Equilibrium Composition for Solar Thermolysis	43
Appendix B. Equilibrium Composition of Ceria	44
References	46

<b>2</b>	<b>Solar Metal Fuels for Future Transportation</b>	<b>65</b>
	<i>Youssef Berro and Marianne Balat-Pichelin</i>	
2.1	Introduction	66
2.1.1	Sustainable Strategies to Address Climate Change	66
2.1.2	Circular Economy	66
2.1.3	Sustainable Solar Recycling of Metal Fuels	68
2.2	Direct Combustion of Solar Metal Fuels	69
2.2.1	Stabilized Metal-Fuel Flame	70
2.2.2	Combustion Engineering	71
2.2.3	Designing Metal-Fueled Engines	72
2.3	Regeneration of Metal Fuels Through the Solar Reduction of Oxides	75
2.3.1	Thermodynamics and Kinetics of Oxides Reduction	75
2.3.2	Effect of Some Parameters on the Reduction Yield	77
2.3.2.1	Carbon-Reducing Agent	77
2.3.2.2	Catalysts and Additives	78
2.3.2.3	Mechanical Milling	78
2.3.2.4	CO Partial Pressure	79
2.3.2.5	Carrier Gas	79
2.3.2.6	Fast Preheating	79
2.3.2.7	Progressive Heating	80
2.3.3	Reverse Reoxidation of the Produced Metal Powders	80
2.3.4	Reduction of Oxides Using Concentrated Solar Power	81
2.3.5	Solar Carbothermal Reduction of Magnesia	83
2.3.6	Solar Carbothermal Reduction of Alumina	86
2.4	Conclusions	89
	Acknowledgments	90
	References	90
<b>3</b>	<b>Design Optimization of a Solar Fuel Production Plant by Water Splitting With a Copper-Chlorine Cycle</b>	<b>97</b>
	<i>Samane Ghandehariun, Shayan Sadeghi and Greg F. Naterer</i>	
	Nomenclature	98
3.1	Introduction	100
3.2	System Description	108
3.3	Mathematical Modeling and Optimization	113
3.3.1	Energy and Exergy Analyses	113
3.3.2	Economic Analysis	116
3.3.3	Multiobjective Optimization (MOO) Algorithm	120



3.4	Results and Discussion	121
3.5	Conclusions	130
	References	131
<b>4</b>	<b>Diversifying Solar Fuels: A Comparative Study on Solar Thermochemical Hydrogen Production Versus Solar Thermochemical Energy Storage Using <math>\text{Co}_3\text{O}_4</math></b>	<b>137</b>
	<i>Atalay Calisan and Deniz Uner</i>	
4.1	Introduction	137
4.2	Materials and Methods	141
4.3	Thermodynamics of Direct Decomposition of Water	142
4.4	A Critical Analysis of Two-Step Thermochemical Water Splitting Cycles Through the Red/Ox Properties of $\text{Co}_3\text{O}_4$	143
4.4.1	Red/Ox Characteristics of $\text{Co}_3\text{O}_4$ Measured by Temperature-Programmed Analysis	145
4.4.2	The Role of Pt as a Reduction Promoter of $\text{Co}_3\text{O}_4$	147
4.4.3	A Critical Analysis of the Solar Thermochemical Cycles of Water Splitting	149
4.5	Cyclic Thermal Energy Storage Using $\text{Co}_3\text{O}_4$	151
4.5.1	Mass and Heat Transfer Effects During Red/Ox Processes	152
4.5.2	Cyclic Thermal Energy Storage Performance of $\text{Co}_3\text{O}_4$	152
4.6	Conclusions	157
	Acknowledgements	157
	References	157
	<b>Part II: Artificial Photosynthesis and Solar Biofuel Production</b>	<b>161</b>
<b>5</b>	<b>Shedding Light on the Production of Biohydrogen from Algae</b>	<b>163</b>
	<i>Thummala Chandrasekhar and Vankara Anuprasanna</i>	
5.1	Introduction	164
5.2	Hydrogen or Biohydrogen as Source of Energy	165
5.3	Hydrogen Production From Various Resources	167
5.4	Mechanism of Biological Hydrogen Production from Algae	168
5.5	Production of Hydrogen from Different Algal Species	171
5.5.1	Generation of Hydrogen in <i>Scenedesmus obliquus</i>	171
5.5.2	Production of Hydrogen in <i>Chlorella vulgaris</i>	174

5.5.3	Generation of Hydrogen in Model Alga <i>Chlamydomonas reinhardtii</i>	175
5.6	Concluding Remarks	177
	Acknowledgments	177
	References	177
<b>6</b>	<b>Photoelectrocatalysis Enables Greener Routes to Valuable Chemicals and Solar Fuels</b>	<b>185</b>
	<i>Dipesh Shrestha, Kamal Dhakal, Tamlal Pokhrel, Achyut Adhikari, Tomas Hardwick, Bahareh Shirinfar and Nisar Ahmed</i>	
6.1	Introduction	186
6.2	C–H Functionalization in Complex Organic Synthesis	189
6.3	Examples of Photoelectrochemical-Induced C–H Activation	190
6.4	C–C Functionalization	192
6.5	Electrochemically Mediated Photoredox Catalysis (e-PRC)	194
6.6	Interfacial Photoelectrochemistry (iPEC)	197
6.7	Reagent-Free Cross Dehydrogenative Coupling	199
6.8	Conclusion	199
	References	200
	<b>Part III: Photocatalytic CO<sub>2</sub> Reduction to Fuels</b>	<b>205</b>
<b>7</b>	<b>Graphene-Based Catalysts for Solar Fuels</b>	<b>207</b>
	<i>Zhou Zhang, Maocong Hu and Zhenhua Yao</i>	
7.1	Introduction	208
7.2	Preparation of Graphene and Its Composites	209
7.2.1	Preparation of Graphene (Oxide)	209
7.2.2	Preparation of Graphene-Based Photocatalysts	210
7.2.2.1	Hydrothermal/Solvothermal Method	211
7.2.2.2	Sol-Gel Method	212
7.2.2.3	<i>In Situ</i> Growth Method	212
7.3	Graphene-Based Catalyst Characterization Techniques	214
7.3.1	SEM, TEM, and HRTEM	214
7.3.2	X-Ray Techniques: XPS, XRD, XANES, XAFS, and EXAFS	215
7.3.3	Atomic Force Microscopy (AFM)	217
7.3.4	Fourier Transform Infrared Spectroscopy (FTIR)	218
7.3.5	Other Technologies	219
7.4	Graphene-Based Catalyst Performance	220
7.4.1	Photocatalytic CO <sub>2</sub> Reduction	223

7.4.2	Hydrogen Production by Water Splitting	229
7.5	Conclusion and Future Opportunities	235
	Acknowledgments	237
	References	237
<b>8</b>	<b>Advances in Design and Scale-Up of Solar Fuel Systems</b>	<b>247</b>
	<i>Ashween Virdee and John Andresen</i>	
8.1	Introduction	248
8.2	Strategies for Solar Photoreactor Design	248
8.2.1	Photocatalytic Systems	249
8.2.1.1	Slurry Photoreactor	252
8.2.1.2	Fixed Bed Photoreactor	254
8.2.1.3	Twin Photoreactor (Membrane Photoreactor)	256
8.2.1.4	Microreactor	259
8.2.2	Electrochemical System	260
8.2.2.1	CO <sub>2</sub> Electrochemical Reactors	263
8.2.3	Photoelectrochemical (PEC) Systems	267
8.3	Design Considerations for Scale-Up	272
8.4	Future Systems and Large Reactors	274
8.5	Conclusions	276
	References	277
	<b>Part IV: Solar-Driven Water Splitting</b>	<b>285</b>
<b>9</b>	<b>Photocatalyst Perovskite Ferroelectric Nanostructures</b>	<b>287</b>
	<i>Debashish Pal, Dipanjan Maity, Ayan Sarkar and Gobinda Gopal Khan</i>	
9.1	Introduction	288
9.2	Ferroelectric Properties and Materials	289
9.3	Fundamental of Photocatalysis and Photoelectrocatalysis	290
9.3.1	Photocatalytic Production of Hydrogen Fuel	290
9.3.2	Photoelectrocatalytic Hydrogen Production	291
9.3.3	Photocatalytic Dye/Pollutant Degradation	292
9.4	Principle of Piezo/Ferroelectric Photo(electro)catalysis	292
9.5	Ferroelectric Nanostructures for Photo(electro)catalysis	294
9.6	Synthesis and Design of Nanostructured Ferroelectric Photo(electro)catalysts	295
9.6.1	Hydrothermal/Solvothermal Methods	295
9.6.2	Sol-Gel Methods	300
9.6.3	Wet Chemical and Solution Methods	303

9.6.4	Vapor Phase Deposition Methods	305
9.6.5	Electrospinning Methods	306
9.7	Photo(electro)catalytic Activities of Ferroelectric Nanostructures	307
9.7.1	Photo(electro)catalytic Activities of BiFeO <sub>3</sub> Nanostructures and Thin Films	307
9.7.2	Photo(electro)catalytic Activities of LaFeO <sub>3</sub> Nanostructures	311
9.7.3	Photo(electro)catalytic Activities of BaTiO <sub>3</sub> Nanostructures	314
9.7.4	Photo(electro)catalytic Activities of SrTiO <sub>3</sub> Nanostructures	317
9.7.5	Photo(electro)catalytic Activities of YFeO <sub>3</sub> Nanostructures	319
9.7.6	Photo(electro)catalytic Activities of KNbO <sub>3</sub> Nanostructures	319
9.7.7	Photo(electro)catalytic Activities of NaNbO <sub>3</sub> Nanostructures	322
9.7.8	Photo(electro)catalytic Activities of LiNbO <sub>3</sub> Nanostructures	323
9.7.9	Photo(electro)catalytic Activities of PbTiO <sub>3</sub> Nanostructures	323
9.7.10	Photo(electro)catalytic Activities of ZnSnO <sub>3</sub> Nanostructures	325
9.8	Conclusion and Perspective	327
	References	329
<b>10</b>	<b>Solar-Driven H<sub>2</sub> Production in PVE Systems</b>	<b>341</b>
	<i>Zaki N. Zahran, Yuta Tsubonouchi and Masayuki Yagi</i>	
10.1	Introduction	342
10.2	Approaches for H <sub>2</sub> Production <i>via</i> Solar-Driven Water Splitting	343
10.3	Principle of Designing of PVE Systems for Solar-Driven Water Splitting	348
10.4	Development of PVE Systems for Solar-Driven Water Splitting	352
10.4.1	PVE Systems Based on Si PV Cells	353
10.4.2	PVE Systems Based on Group III-V Compound PV Cells	354
10.4.3	PVE Systems Based on Chalcogenide PV Cells	356
10.4.4	PVE Systems Based on Perovskite PV Cells	358

10.4.5	PVE Systems Based on Organic Heterojunction PV Cells	359
10.5	Conclusions and Future Perspective	361
	References	361
<b>11</b>	<b>Impactful Role of Earth-Abundant Cocatalysts in Photocatalytic Water Splitting</b>	<b>375</b>
	<i>Yubin Chen, Xu Guo, Zhichao Ge, Ya Liu and Maochang Liu</i>	
11.1	Introduction	376
11.2	Categories of Cocatalysts Utilized in Photocatalytic Water Splitting	378
11.2.1	Metal and Non-Metal Cocatalysts	379
11.2.2	Metal Oxides and Hydroxides	380
11.2.3	Metal Sulfides	381
11.2.4	Metal Phosphides and Carbides	382
11.2.5	Molecular Cocatalysts	383
11.3	Factors Determining the Cocatalyst Activity	384
11.3.1	Intrinsic Properties of Cocatalysts	384
11.3.2	Interfacial Coupling of Cocatalysts With Host Semiconductors	388
11.4	Advanced Characterization Techniques for Cocatalytic Process	393
11.5	Conclusion	395
	Acknowledgments	396
	References	396
	<b>Index</b>	<b>411</b>



## Preface

---

Among all other energy sources, solar power is the one with the highest capacity and greatest potential. It is humanity's great loss to not be able to use solar energy to produce all the energy we need. This is particularly true since the environmental and sociopolitical problems caused by the use of fossil fuels have negatively affected our future welfare. Therefore, with this as the motivating factor, basic science and engineering studies have been continuing at a rapid pace with the aim of eliminating existing problems to ensure a more efficient and widespread use of solar energy. The biggest disadvantage that solar energy has to face is that it is not accessible at all times of the day and year; in other words, the energy obtained from the sun must be stored.

The energy from photovoltaic systems can be stored in flow batteries or other battery systems, as well as making it storable by converting solar energy to chemical energy, which will make it more cost-effective and versatile compared to the current method. Synthetic chemical fuels obtained by using solar energy are called solar fuels. Hydrogen, methanol, methane, ammonia, carbon monoxide, and some other hydrocarbons and/or oxygenates can be produced from abundant feedstocks such as water, carbon dioxide, and nitrogen via different solar energy-based routes. These routes include solar thermolysis, artificial photosynthesis, and photocatalytic and photoelectrochemical conversion. Therefore, we organized our book to review these routes in informative chapters submitted by distinguished authors. We, as editors, wish to thank the authors for their valuable contributions. This volume covers cutting-edge technologies and materials for efficient solar fuel generation. Additionally, it highlights the research efforts in the literature and adds a valuable component to the area. In addition to the basics, this book also discusses advanced engineering details for both scientists and engineers in academia and industry.

There are four parts and eleven chapters in the book. Part I, Solar Thermochemical and Concentrated Solar Approaches, includes four chapters. Chapter 1 summarizes hydrogen generation via solar thermolysis.

This chapter focuses on the theoretical methods, the state-of-the-art redox-active metal oxides, next-generation perovskite redox-active materials, and materials design directions. Chapter 2 covers recyclable solar transport fuels. In this chapter, all the important aspects of sustainability of solar metal fuels for future long-distance transportation through combustion/reduction cycles are discussed, including direct combustion of solar metal fuels and regeneration of metal fuels through the solar reduction of oxides. Chapter 3 discusses the design and optimization of a standalone plant for hydrogen generation powered by solar energy. Fundamental advances in the copper-chlorine (Cu-Cl) high-performance thermochemical cycle, thermodynamic and economic analyses, and optimization of the system for two objective functions, including the levelized cost of producing hydrogen and solar-to-hydrogen efficiency, are explained in this chapter. Chapter 4 presents a comparative study on solar thermochemical hydrogen production versus solar heat storage using cobalt oxide ( $\text{Co}_3\text{O}_4$ ). Among the topics covered are the thermodynamics of direct decomposition of water, a critical analysis of two-step thermochemical water splitting cycles through the redox properties of  $\text{Co}_3\text{O}_4$ , and cyclic thermal energy storage using  $\text{Co}_3\text{O}_4$ .

Part II, Artificial Photosynthesis and Solar Biofuel Production, includes two chapters. Chapter 5 covers the production of biohydrogen from algae. Overall, this chapter intends to summarize the developments in hydrogen production from certain algal species, which is helpful for commercial practice in the near future. Chapter 6 summarizes state-of-the-art applications of photoelectrocatalysis (PEC) in the synthesis of valuable chemicals and solar fuels. This chapter focuses on C-H functionalization in complex organic synthesis, examples of photoelectrochemical-induced C-H activation, C-C functionalization, electrochemically mediated photoredox catalysis, interfacial photoelectrochemistry, and reagent-free cross dehydrogenative coupling.

Part III, Photocatalytic  $\text{CO}_2$  Reduction to Fuels, includes two chapters. Chapter 7 focuses on graphene-based catalysts for solar fuels. The preparation of graphene and its composites and the performance of graphene-based catalysts are covered in this chapter. Chapter 8 covers the advances in the design and scale-up of solar fuel systems. Also discussed are strategies for solar photoreactor design, including photocatalytic and electrochemical systems for carbon dioxide reduction, design considerations for scale-up, and future systems and large reactors.

Part IV, Solar-Driven Water Splitting, includes three chapters. Chapter 9 summarizes the advanced materials and systems for solar hydrogen generation. Perovskite ferroelectric nanostructures for photocatalysis



and photoelectrocatalysis are also introduced in this chapter. Chapter 10 focuses on photovoltaic-electrolyzer (PVE) systems, consisting of photovoltaic (PV) cells connected by wires with electrolyzers equipped with an anode and a cathode in an electrolyte solution as one of the most promising approaches for solar-driven water splitting. Finally, Chapter 11 offers meaningful guidance to design cost-effective and highly efficient cocatalysts for photocatalytic water splitting. In this context, the basic working principle of cocatalysts and a summary of extensively studied earth-abundant cocatalysts are provided.

In conclusion, we would like to emphasize that this third volume of the *Advances in Solar Cell Materials and Storage* series provides an overall view of the new and highly promising photoactive materials and system designs for solar fuel generation. Therefore, readers from diverse fields, including chemistry, physics, materials science, engineering, and mechanical and chemical engineering, can definitely take advantage of the information presented in this book to better understand the impacts of solar fuels.

**Series Editors**

**Nurdan Demirci Sankir PhD and Mehmet Sankir PhD**

*Department of Materials Science and Nanotechnology Engineering,  
TOBB University of Economics and Technology*

February 20, 2023



# **Part I**

## **SOLAR THERMOCHEMICAL AND CONCENTRATED SOLAR APPROACHES**



# Materials Design Directions for Solar Thermochemical Water Splitting

Robert B. Wexler<sup>1</sup>, Ellen B. Stechel<sup>2</sup> and Emily A. Carter<sup>1\*</sup>

<sup>1</sup>*Department of Mechanical and Aerospace Engineering and the Andlinger Center for Energy and the Environment, Princeton University, Princeton, NJ, United States*

<sup>2</sup>*ASU LightWorks<sup>®</sup> and the School of Molecular Sciences, Arizona State University, Tempe, Arizona, United States*

---

## **Abstract**

Solar thermochemical water splitting (STWS) offers a renewable route to hydrogen with the potential to help decarbonize several industries, including transportation, manufacturing, mining, metals processing, and electricity generation, as well as to provide sustainable hydrogen as a chemical feedstock. STWS uses high temperatures from concentrated sunlight or other sustainable means for high-temperature heat to produce hydrogen and oxygen from steam. For example, in its simplest form of a two-step thermochemical cycle, a redox-active metal oxide is heated to  $\approx 1700$  to  $2000$  K, driving off molecular oxygen while producing oxygen vacancies in the material. The reduced metal oxide then cools (ideally with the extracted heat recuperated for reuse) and, in a separate step, comes into contact with steam, which reacts with oxygen vacancies to produce molecular hydrogen while recovering the original state of the metal oxide. Despite its promising use of the entire solar spectrum to split water thermochemically, the estimated cost of hydrogen produced via STWS is  $\approx 4$  to  $6\times$  the U.S. Department of Energy (DOE) Hydrogen Shot target value of  $\$1/\text{kg}$ .

One contributing approach to bridging this cost gap is the design of new materials with improved thermodynamic properties to enable higher efficiencies. The state-of-the-art (SOA) redox-active metal oxide for STWS is ceria ( $\text{CeO}_2$ ) because of its close to optimal, although too high, oxygen vacancy formation enthalpy and large configurational and electronic entropy of reduction. However, ceria requires high operating temperatures, and its efficiency is insufficient. Therefore, efforts to increase the efficiency of STWS cycles have focused

---

\*Corresponding author: eac@princeton.edu

on further optimizing oxygen vacancy formation enthalpies and augmenting the reduction entropy via substitution or doping and materials discovery schemes. Examples of the latter include the perovskites  $\text{BaCe}_{0.25}\text{Mn}_{0.75}\text{O}_3$  and  $(\text{Ca,Ce})(\text{Ti,Mn})\text{O}_3$ . These efforts and others have revealed intuitive chemical principles for the efficient and systematic design of more effective materials, such as the strong correlation between the enthalpies of crystal bond dissociation and solid-state cation reduction with the enthalpy of oxygen vacancy formation, as well as configurational entropy augmentation via the coexistence of two or more redox-active cation sublattices.

The purpose of this chapter is to prepare the reader with an up-to-date account of STWS redox-active materials, both the SOA and promising newcomers, as well as to provide chemically intuitive strategies for improving their cycle efficiencies through materials design—in conjunction with ongoing efforts in reactor engineering and gas separations—to reach the cost points for commercial viability.

**Keywords:** Climate change, concentrated solar technologies, hydrogen, solar thermolysis, solar thermochemical cycles, redox-active materials, off-stoichiometric, quantum mechanics simulations

## 1.1 Introduction

Combatting anthropogenic climate change is one of the critical scientific and engineering challenges of our time. The associated global warming (Figure 1.1a)—predominantly brought about by greenhouse-gas emissions from burning fossil fuels [1–3]—already has led to extreme weather events that threaten the safety and food/water security of life on Earth. Averting the most disastrous effects of climate change calls—at least in part—for clean fuel alternatives to avoid the  $\text{CO}_2$  emissions from hard-to-electrify sectors, including heavy-duty vehicles with petroleum-based combustion engines. One encouraging alternative is  $\text{H}_2$ , which has a higher-energy density per unit mass than liquid hydrocarbons and can be produced using sustainable energy in the form of concentrated solar heat via thermolysis or thermochemical water splitting (Figure 1.1b) [4]. Although not reviewed here,  $\text{H}_2$  can also be sustainably produced from water by alternative means, for example, via photoelectrochemical water splitting [5, 6] and both high- [7] and low-temperature [8] electrolysis employing renewable (or nuclear) energy. Concentrated solar technologies (CSTs) also promise to reduce the

carbon dioxide footprint of fossil-fuel-derived  $H_2$  from steam-methane reforming, hydrocarbon (fossil or biomass) gasification, solid-oxide electrolysis, and methane cracking.

Two popular solar thermal collector/receiver/reactor designs are the tower with a heliostat field and the parabolic dish (Figure 1.1c) [9]. In the increasingly adopted solar power tower plant architecture, many heliostats focus sunlight on an elevated receiver, achieving a solar concentration ratio ( $C$ )—i.e., the factor by which a collector/receiver multiplies the intensity of sunlight impinging upon the Earth's surface—of  $\approx 1000$ . For parabolic dishes, a polished metal mirror lining concentrates sunlight on a focal point, where redox-active materials could be heated to high temperatures (e.g., 1700–1800 K [10]). While dishes currently are more expensive than towers, they generally lead to a higher  $C$  [11] and recently have been used in demonstration CST-based systems [10].

The theoretical maximum efficiency of solar-to- $H_2$  conversion using CSTs is—under the assumption of ideal optics and a perfectly insulated receiver—the product of the solar collector, receiver, and reactor (Carnot) efficiencies [12, 13]

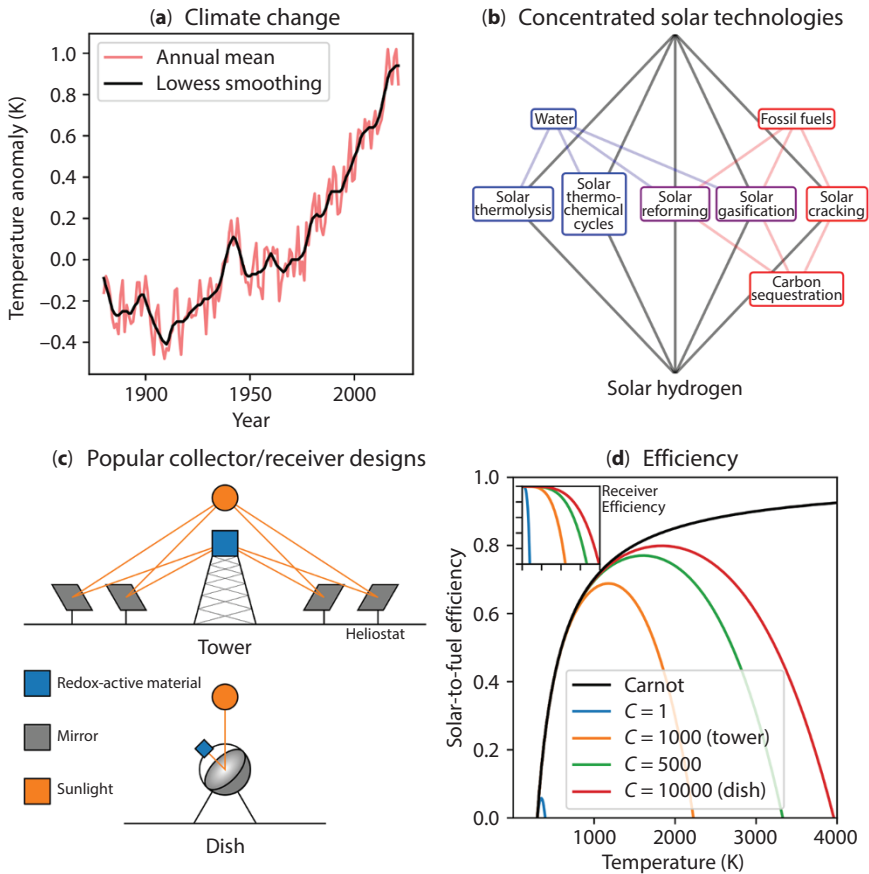
$$\eta_{solar-to-fuel} = \eta_{collector} \eta_{receiver} \eta_{Carnot} \quad (1.1)$$

$$\eta_{receiver} = 1 - \frac{\sigma T^4}{IC} \quad (1.2)$$

$$\eta_{Carnot} = 1 - \frac{T_{sur}}{T} \quad (1.3)$$

where  $\sigma$  is the Stefan–Boltzmann constant;  $T$  the temperature of the receiver;  $I$  the intensity of the direct, normal-incident sunlight; and  $T_{sur}$  is the temperature of the surroundings (e.g., 298.15 K). Suppose a heliostat field with a solar tower is used instead of a parabolic dish. In that case,  $\eta_{collector}$  will be less than one due to factors including the cosine effect (i.e., due to heliostats not pointing directly at the sun and the receiver simultaneously, hence, there is a reduction in the effective reflection area) [14]. One can think of the receiver efficiency ( $\eta_{receiver}$ ) as the fraction of absorbed

sunlight that is not reradiated by the blackbody-like receiver. Increasing  $C$  can increase the  $T$  range over which  $\eta_{\text{receiver}}$  is close to 100%. For example, if parabolic dishes—with  $C$  reaching 10000—can be made economical, then a nearly perfect receiver can be achieved at  $\approx 2000$  K (Figure 1.1d,



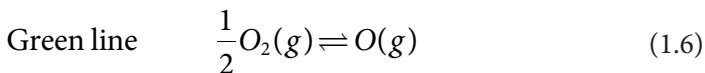
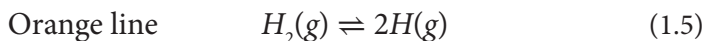
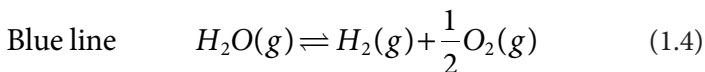
**Figure 1.1** Concentrated solar hydrogen for combatting climate change. (a) Increase in global temperature since 1880. (b) Routes to solar hydrogen via concentrated solar technologies. (c) Popular collector/receiver designs for concentrated solar heat technologies. (d) Ideal solar-to-fuel efficiency ( $\eta_{\text{solar-to-fuel}}$  in Equation (1.1)) and (d, inset) receiver efficiency ( $\eta_{\text{receiver}}$  in Equation (1.2))—with the same ticks and tick labels as the larger panel). Note that towers can have  $C > 1000$  and developing dishes with  $C = 10,000$  is quite challenging. That said, we chose these values to indicate the effect of order-of-magnitude changes in  $C$  on the theoretical solar-to-fuel efficiency.



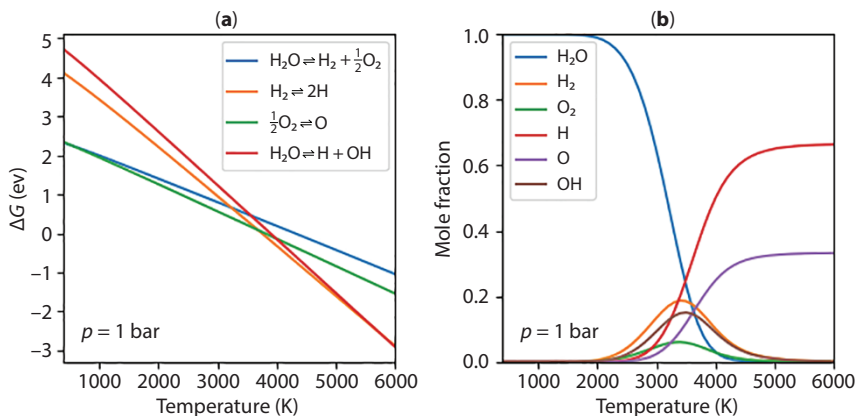
inset). While  $\eta_{\text{receiver}}$  dominates  $\eta_{\text{solar-to-fuel}}$  in the high-temperature limit, the efficiency of a Carnot engine ( $\eta_{\text{Carnot}}$ ) governs the low-temperature regime, which decreases to zero as  $T$  approaches  $T_{\text{sur}}$  from above. Upon multiplying these three efficiencies, it becomes clear that—for a given  $C$ —there is an ideal temperature at which  $\eta_{\text{solar-to-fuel}}$  is maximized (Figure 1.1d). As an example, consider a dish that provides  $C = 5000$ . If the receiver is heated to 1800 K, one can use  $\leq 76\%$  of the concentrated sunlight energy for solar-to- $\text{H}_2$  conversion. Here, the “less than” indicates that other loss mechanisms and engineering constraints typically produce efficiencies  $\ll 76\%$ .

### 1.1.1 Hydrogen via Solar Thermolysis

Having introduced CSTs and their efficiencies for a general solar-to- $\text{H}_2$  process, we now consider the earliest and perhaps simplest approach to CST-based hydrogen production via solar thermolysis or *direct* solar water splitting [15]. In solar thermolysis,  $\text{H}_2\text{O}(\text{g})$  is heated to  $T \geq 2500$  K, above which it can undergo the following high-temperature reactions (Figure 1.2a) [16]:



At  $T < 2000$  K and  $p = 1$  bar, none of these reactions occur with appreciable yields, leaving  $\text{H}_2\text{O}(\text{g})$  intact (Figure 1.2b). As  $T$  reaches 2500 K,  $\approx 4\%$  of  $\text{H}_2\text{O}(\text{g})$  molecules split into  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$  (Equation 1.4). For  $T > 2500$  K, however, side reactions—such as the atomization of  $\text{H}_2(\text{g})$  (Equation 1.5) and  $\text{O}_2(\text{g})$  [Equation (1.6)], and the dissociation of  $\text{H}_2\text{O}(\text{g})$  into  $\text{H}(\text{g})$  and  $\text{OH}(\text{g})$  (Equation 1.7)—compete with the desired water-splitting reaction, leading to a maximum  $\text{H}_2(\text{g})$  mole fraction of  $\approx 0.19$  at 3400 K. In addition to its upper limit for  $\text{H}_2$  generation, solar thermolysis is impractical [17] because it produces an explosive mixture of  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$  that requires careful separation and rapid quenching to avoid recombination, which reduces efficiency. Furthermore, the  $T$  needed to produce  $\text{H}_2(\text{g})$  and not

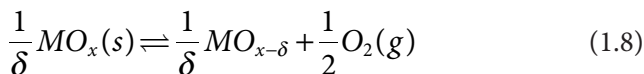


**Figure 1.2** Thermodynamics of hydrogen production via solar thermolysis. (a) Gibbs free energy change ( $\Delta G$ ) of high-temperature reactions at  $p = 1$  bar. (b) Equilibrium mole fractions at  $p = 1$  bar (see Appendix A. Equilibrium Composition for Solar Thermolysis).

$\text{H}(\text{g})$  or  $\text{OH}(\text{g})$ —i.e.,  $\approx 2500$  K—leads to the thermal failure of the ceramics used for  $\text{H}_2(\text{g})$  and  $\text{O}_2(\text{g})$  separation, thus motivating—in the absence of solutions for these issues—another route to solar  $\text{H}_2$ , namely solar thermochemical water splitting (STWS) [18–26].

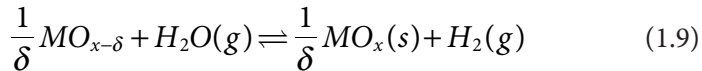
### 1.1.2 Hydrogen via Solar Thermochemical Cycles

To split water at lower temperatures and preclude the formation of undesired gas-phase molecules, one can employ thermochemical cycles, the simplest of which—and the primary subject of this book chapter—is a two-step cycle [27–34] (Figure 1.3a) with redox-active, metal-oxide materials (Figure 1.3b). In such a cycle, a metal oxide ( $\text{MO}_x$ , where  $x$  is the number of moles of O per cation) first is heated, using CSTs, to temperatures typically exceeding 1500 K and most often close to 1800 K, at which point it is reduced to a more O-poor stoichiometry ( $\text{MO}_{x-\delta}$ ), i.e.,



where  $\delta$  is the off-stoichiometry; note that we have purposefully omitted the phase of the reduced metal oxide for reasons to be explained momentarily. Generally speaking, one would reduce at the highest temperatures within engineering and economic constraints to ensure maximal reduction

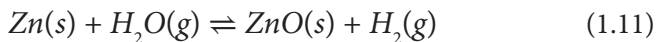
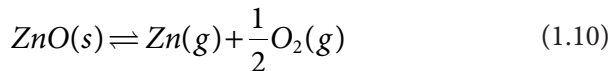
(as increasing the temperature makes  $\Delta G$  more negative and therefore increases  $\delta$ ) and fast kinetics. In the second step, the reduced metal oxide cools to a temperature where reoxidation is possible when exposed to  $H_2O(g)$ , which leads to water splitting and regeneration of the original metal oxide, i.e.,



Generally,  $MO_{x-\delta}$  will not reoxidize to the fully stoichiometric form  $MO_x$  but will cycle between two forms of the metal-oxide stoichiometry—both partially reduced—where the difference between the two off-stoichiometries is one of the performance metrics. The reoxidation is further limited if there is a small amount of hydrogen in the gas stream, which might be expected if one separates, in the gas phase, the hydrogen from the reoxidation product stream and recycles any unconverted steam.

Unlike thermal reduction (Equation 1.8), whose ideal operating temperature is bounded only from above by the thermal stability of the material and durability of the reactor, one would perform water splitting (Equation 1.9) at temperatures high enough for fast kinetics but low enough for a good  $\Delta G$  of reoxidation. This compromise often requires water splitting to be done around 1000 K or higher. Another consideration is recuperation of heat between the high temperature and low temperature steps. The larger the temperature difference, the greater the engineering challenge to limit the losses.

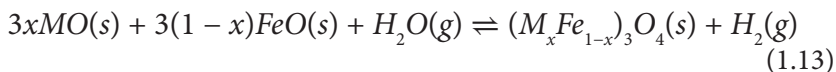
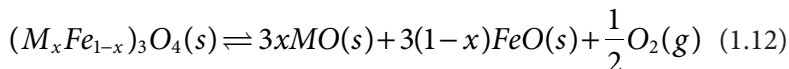
Until now, we have neither specified the phase of  $MO_{x-\delta}$  nor the extent of reduction  $\delta$ . Two-step metal-oxide thermochemical cycles are based on either volatile or non-volatile metal oxides. Volatile refers to a metal oxide for which a solid-to-gas phase transition accompanies thermal reduction. One of the most widely studied volatile cycles is  $ZnO(s)/Zn(g)$  [35–37]:



In the thermal reduction step [Equation (1.10)], which one must carry out at temperatures above 2000 K,  $ZnO(s)$  volatilizes to  $Zn(g)$  and  $O_2(g)$ . While the  $ZnO(s)/Zn(g)$  cycle offers favorable efficiencies even in the

absence of heat recovery (energy conversion efficiency  $\approx 45\%$  and maximum exergy efficiency  $\approx 29\%$ ), its issues are similar to those faced in solar thermolysis in that the high temperatures required for significant reduction put a considerable thermal strain on the receiver/reactor [17, 38]. After thermal reduction, one generally quenches quickly to avoid the back reaction before separating Zn(s) from O<sub>2</sub>(g). Alternatively, electrothermal gas-phase separation has been considered [39, 40]. Water splitting [Equation (1.11)], on the other hand, typically takes place at  $T \leq 900$  K, revealing another difficulty for ZnO(s)/Zn(g): the need for a giant temperature swing ( $\geq 1100$  K). Other redox couples for volatile, two-step STWS have been considered, such as post-transition-metal oxides in the SnO<sub>2</sub>(s)/SnO(g) cycle [41–43]; however, those with greater attention currently are solid phase, a.k.a. non-volatile, redox-active materials.

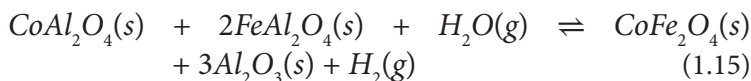
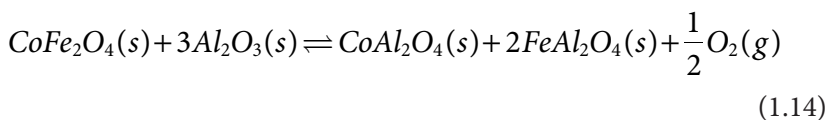
Within non-volatile, redox-active metal oxides, the two main categories are stoichiometric (line compounds) and off-stoichiometric. First, we consider stoichiometric metal oxides, where stoichiometric refers to materials for which reduction and reoxidation produce pure, solid-phase, metal-containing compounds obeying full stoichiometry constraints on composition. One can further subdivide stoichiometric metal oxides into single-component and multi-component compositions. Examples best illustrate the difference between these two types of stoichiometric oxides. The prototypical single-component materials are metal-doped ferrites [44–54], whose thermal reduction and water splitting reactions are



where the metal (M) dopant or substituent can be Fe (in which case Fe is not a dopant and the phase is magnetite) [55–59], Zn [60], Ni [60, 61], Co [60, 62] (as well as a complete replacement of Fe with Co [63]), Mn [61], and others. Ferrites with other metals substituted in the spinel or inverse spinel structure can be tuned to provide nearly optimal reduction Gibbs free energetics and reduction temperatures lower than 2000 K [64, 65]. However, both their reduction and water-splitting kinetics are slow because O<sup>2-</sup> is close-packed in both oxide structures, Fe<sub>3</sub>O<sub>4</sub> and FeO(s). Therefore, it does not react beyond the surface [66]. Additionally, powdered Fe oxides sinter, rendering them uncyclable [56, 62, 67, 68]. To enhance cyclability,

one can use yttria-stabilized zirconia as an inert support that incorporates active Fe ions into its crystal lattice, forming a solid solution, thus alleviating the sintering or melting of iron oxides at the working temperatures of 1200 to 1700 K [55, 69]. Note that, for ferrite cycles, a single metal oxide reduces and reoxidizes, hence the terminology “single component.”

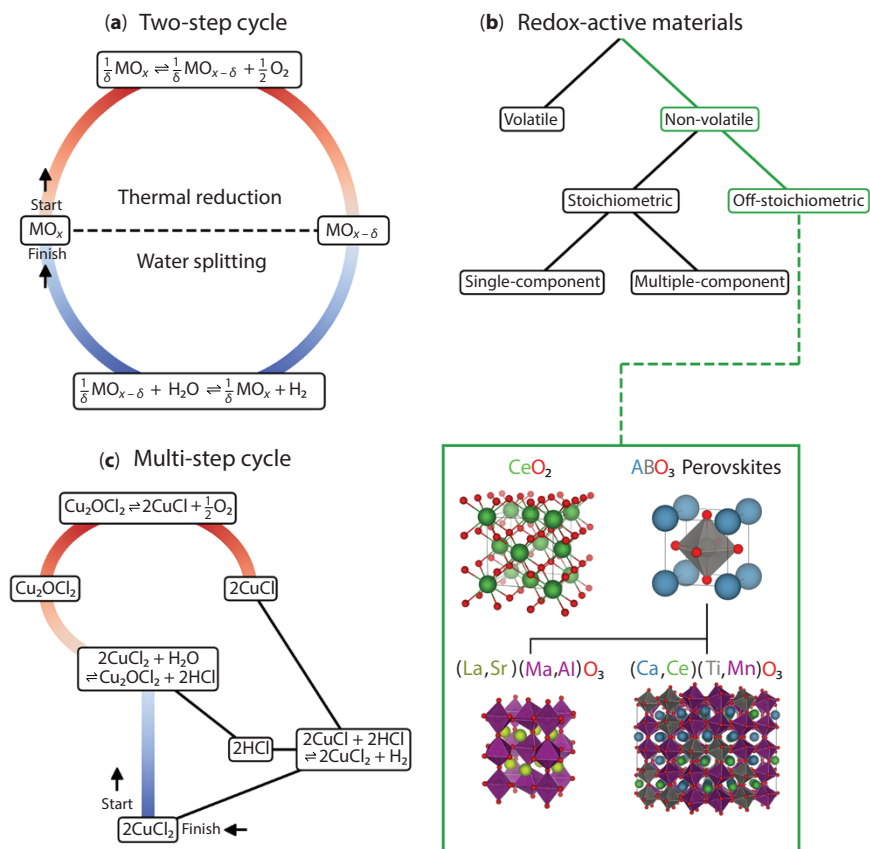
Alternatively, multi-component cycles involve the redox of more than one metal oxide component. An excellent example of this case is the cycle based on the mineral hercynite  $\text{FeAl}_2\text{O}_4(\text{s})$  [70–77]:



During thermal reduction,  $\text{CoFe}_2\text{O}_4(\text{s})$ —a metal-substituted ferrite—reacts with three moles of  $\text{Al}_2\text{O}_3(\text{s})$ , producing  $\text{CoAl}_2\text{O}_4(\text{s})$ —a pigment known as cobalt blue—along with two moles of hercynite and a half mole of  $\text{O}_2(\text{g})$ . These intermediate products then split water at lower temperatures, restoring the original solids in their starting stoichiometric coefficients and generating  $\text{H}_2(\text{g})$ . Both steps have two metal-oxide components in the reactants and products, so the hercynite cycle is multi-component. However, like the ferrites, this cycle suffers from poor kinetics, which is unsurprising considering one of the components is cobalt ferrite  $\text{CoFe}_2\text{O}_4(\text{s})$ . Other studied multicomponent cycles include—but are not limited to—those based on the metal sulfate/oxide [e.g.,  $\text{MnSO}_4(\text{s})/\text{MnO}(\text{s})$  [78]] and metal dioxide/pyrochlore [i.e.,  $\text{CeO}_2(\text{s})+\text{MO}_2(\text{s})/\text{Ce}_2\text{M}_2\text{O}_7(\text{s})$  where M can be, e.g., Ti [79], Si [79], or Sn [80]] redox couples. Ultimately, kinetic limitations are a hallmark of stoichiometric materials because their STWS cycles require the nucleation and growth of bulk phases. A promising path to promote faster kinetics is to use off-stoichiometric metal oxides, which tend to be mixed ionic-electronic conductors (MIECs) that form and fill oxygen vacancies ( $\text{V}_{\text{O}}$ s) during thermal reduction and water splitting, respectively, instead of undergoing major bulk structural phase transitions. As off-stoichiometric metal oxides, particularly MIECs because of their superior ion diffusion kinetics, currently are the subject of intense research for STWS applications and are the redox-active materials of choice for pilot plants, we focus on them here. Below we emphasize developing intuition that explains observed physicochemical phenomena, in order to determine

materials design criteria that can lead to tailoring materials for more optimal thermochemical cycles.

Before we dive into the details of off-stoichiometric metal oxides for STWS, we would be remiss if we did not mention the utility of multi-step cycles. We will first describe the Cu-Cl [81] cycle (Figure 1.3c). In the hydrolysis step,  $\text{Cu(II)Cl}_2(\text{s})$  is heated to  $\approx 673$  K in the presence of  $\text{H}_2\text{O}(\text{g})$ ,



**Figure 1.3** Hydrogen production via solar thermochemical cycles. (a) Schematic of a two-step cycle for a metal oxide ( $\text{MO}_x$ ) that becomes off-stoichiometric ( $\text{MO}_{x-\delta}$ , where  $\delta$  is the off-stoichiometry) upon thermal reduction (where the color of the circle denotes relative temperature). (b) Types of redox-active materials typically employed for two-step STWS, where our focus is on nonvolatile materials that become off-stoichiometric upon thermal reduction, such as  $\text{CeO}_2$  and  $\text{ABO}_3$  perovskites and their alloys. (c) Schematic of a multistep cycle, specifically, here, the copper chloride hybrid cycle, which involves hydrolysis (blue), thermal reduction (red), and electrolysis (black) steps at different temperatures.