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Aneeya Kumar Samantara • Satyajit Ratha

Metal Oxides/Chalcogenides and Composites

Emerging Materials for Electrochemical Water Splitting

Springer

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*Dr. Aneeya Kumar Samantara would like to dedicate this work to
his parents, Mr. Braja Bandhu Dash and Mrs. Swarna Chandrika Dash, and his beloved wife, Elina.*

*Dr. Satyajit Ratha would like to dedicate this work to
his parents, Mrs. Prabhati Ratha and Mr. Sanjaya Kumar Ratha.*

Preface

With its high specific energy, zero emission, and lightweight nature, hydrogen can lead the green energy revolution. Internal combustion engines running on hydrogen fuel cells have at least twofold higher specific energy than those running on gasoline. Therefore, hydrogen storage is highly essential for next-generation transportation fuel, considering the depleting fossil fuel reserves (and adverse effects arising from their combustion), thus escalating its industrial necessity. However, the limited reserve of hydrogen in the atmosphere has long been a limiting factor to realize hydrogen energy at large scale. In this context, splitting of water through electrochemical processes or solar power-driven techniques is paving the way for next-generation hydrogen production. Similar approach has also been taken toward the production of oxygen which helps in the combustion of hydrogen in hydrogen fuel cells and is also vital for the metal-air battery systems. State-of-the-art catalysts for hydrogen evolution reaction (Pt/C), and oxygen evolution reaction (IrO_2), make use of precious metals and thus are not suitable for industrial-scale production of both hydrogen and oxygen. However, several reports have tried to address the typical challenge to find the low-cost alternatives for these precious metal-based catalysts. Large-scale water splitting is essential not only for sustainable growth, promoting green energy, but also to reduce both carbon footprint and greenhouse gases. Photoelectrochemical water splitting is an effective and promising method to produce hydrogen and oxygen from water. A wide variety of metal-based compounds, especially compounds having core cations from the transition (or d-block) group, have been investigated for their feasibility to be used as efficient catalysts for water splitting reactions. These include carbon-based nanocomposites (metal-free catalysts), metal chalcogenides, oxides, phosphides, borides, carbides, nitrides, hydroxides, and so forth. Transition metal chalcogenides, as low-cost alternatives, have performed well as hydrogen evolution reaction (HER) catalysts. Their stability issues, however, still possess stiff challenges for the batch production process of hydrogen. In this context, metal oxide-based compounds have been investigated over the years along with the metal chalcogenides, and these oxide materials have been found to possess excellent stability even for over thousands of reaction cycles. Several other materials that have been mentioned, e.g., metal phosphides, borides, carbides, etc., have also been implemented as electrocatalysts for HER.

This brief provides a detailed emphasis on the fundamentals of the water splitting process, underlying mechanism, and a niche of catalyst materials/composites to showcase their effectiveness toward both cost optimization and stability. Also, a rigorous comparison has been drawn to show the versatile nature of these catalytic compounds that can provide sufficient flexibility to facilitate the hydrogen production process.

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About the Book

Hydrogen as fuel has a significant role to play in sustainable growth and as energy carrier can decarbonize the energy sector, both at household and industrial level. The current hydrogen economy is not promising, considering few strategic bottlenecks such as the methods used for hydrogen production, storage, and transportation. Also, the move from gray hydrogen to green hydrogen is not going to be an easy task as these projects are still at a nascent stage (though laboratory-scale productions have been technically proven). Thus, to see hydrogen as a clean and carbon-free source of fuel and as an industrial commodity, focus should be shifted toward the hydrogen generation from water through electrolysis technique. Though can be costly at initial stages, electrolysis through electrolyzers can solve both small- and large-scale energy requirements.

This book provides a detailed emphasis on the role of electrolysis for hydrogen production and materials that could prove significant to catalyze the electrolysis process. Various metal compounds such as metal oxides, sulfides, carbides, and phosphides and few carbon-based nonmetallic compounds have been scrutinized for their effectiveness in promoting the hydrogen evolution during water splitting process. These low-cost metallic/carbonaceous materials provide a wide range of alternatives to the state-of-the-art catalyzers based on precious metal components such as Pt and Ir, which could make the concept of hydrogen, being a sustainable fuel and energy carrier, realistic. This is critical for sustainable growth by limiting the consumption of fossil fuels, curbing greenhouse gases like CO_2, and achieving 100% decarbonized energy generation.

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About the Authors

Aneeya Kumar Samantara is presently working as a postdoctorate fellow at the *School of Chemical Sciences, National Institute of Science Education and Research*, Khordha, Odisha, India. He pursued his PhD at *CSIR-Institute of Minerals and Materials Technology*, Bhubaneswar, Odisha, India. Before joining the PhD, he completed the Master of Philosophy (MPhil) in Chemistry from *Utkal University* and Master in Science in *Advanced Organic Chemistry* at *Ravenshaw University*, Cuttack, Odisha. His research interest includes the synthesis of metal oxide/chalcogenides and graphene composites for energy storage and conversion application. To his credit, he has authored 21 peer-reviewed international journals, 6 books (2 books in Springer, 2 in Arcler Press, and 2 in Global Publishing House, India), and 4 book chapters. Four books and two research journals are in press and will probably be published soon.

Satyajit Ratha pursued his PhD at the School of Basic Sciences, Indian Institute of Technology Bhubaneswar, India. Prior to joining IIT Bhubaneswar, he received his Bachelor of Science, First Class Honors, from Utkal University in 2008 and Master of Science from Ravenshaw University in 2010. His research interests include two-dimensional semiconductors, nanostructure synthesis, applications, energy storage devices, and supercapacitors. He has authored and coauthored about 20 peer-reviewed international journals and 4 books (2 in Springer and 2 in Arcler Press).

Abbreviations

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
BET	Brunauer-Emmett-Teller
BMW	Bayerische Motoren Werke
BSCF	$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$
BTMPs	Binary metal phosphide
CAES	Compressed air energy storage
CCS	Carbon capture and storage
C_{dl}	Double-layer capacitance
CE	Counter electrode
CFP	Carbon fiber paper
CNT	Carbon nanotube
CPE	Constant phase element
CV	Cyclic voltammogram
CVD	Chemical vapor deposition
DFT	Density functional theory
DHE	Dynamic hydrogen electrode
DPs	Double perovskites
ECSA	Electrochemical active surface area
EIS	Electrochemical impedance spectroscopy
EXAFS	Extended X-ray absorption fine structure
FCEV	Fuel cell electric vehicles
FE	Faradic efficiency
FFT	Fast Fourier transforms
HAADF	High-angle annular dark-field
HER	Hydrogen evolution reaction
HRTEM	High-resolution transmission electron microscope
LDH	Layered double hydroxide
LSV	Linear sweep voltammogram
MOF	Metal organic framework

NCO	$NiCo_2O_4$
NHE	Normal hydrogen electrode
NPCC	N, P-codoped carbon shell
NREL	National Renewable Energy Laboratory
NRs	Nano rods
NSs	Nano sheets
NWs	Nano wires
OCP	Open circuit potential
OER	Oxygen evolution reaction
PCN	Phosphorus-doped graphitic carbon nitride
PEM	Polymer electrolyte membrane
PVD	Physical vapor deposition
RDS	Rate determining step
RE	Reference electrode
RG	Reduced graphene oxide
RHE	Reversible hydrogen electrode
RRDE	Rotating ring disk electrode
SCE	Saturated calomel electrode
SEM	Scanning electron microscope
S_{geo}	Geometrical surface area
$S_{geo.}$	Geometrical surface area
SMR	Steam methane reforming
STEM	Scanning tunneling electron microscope
TMC	Transition metal chalcogenide
TMN	Transition metal nitride
TMO	Transition metal oxide
TMP	Transition metal phosphide
TMPS	Transition metal phosphosulfide
TOF	Turnover frequency
UPS	Ultraviolet photoemission spectroscopy
WE	Working electrode
XAS	X-ray absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Abstract This book presents a brief discussion on issues of traditional energy resources and types of nonrenewable/alternative energy resources. As an efficient device, more focus has been given to electrolyzers. Further fundamental discussion on different parameters used to evaluate performance of an electrocatalyst is elaborately presented, followed by emergence of different electrocatalysts. Although the noble metal-based catalysts perform efficiently, their high cost and limited reserve motivate the researchers to think some alternatives. In this regard, low-cost transition metal-based electrocatalysts and composites with different conductive carbon materials were developed, but their catalytic activity yet remained far from that shown by the noble metals. Therefore, discussion on the synthesis, mechanism study, and catalytic performance of different electrocatalysts suitable for electrolyzer has been emphasized. The authors presume that this book will help the energy and materials researchers to gather more knowledge in this field and to explore new electrocatalysts with higher efficiencies for commercial application.

Keywords Electrolyzer · Hydrogen evolution · Oxygen evolution reaction · Energy conversion · Metal oxides · Metal chalcogenides