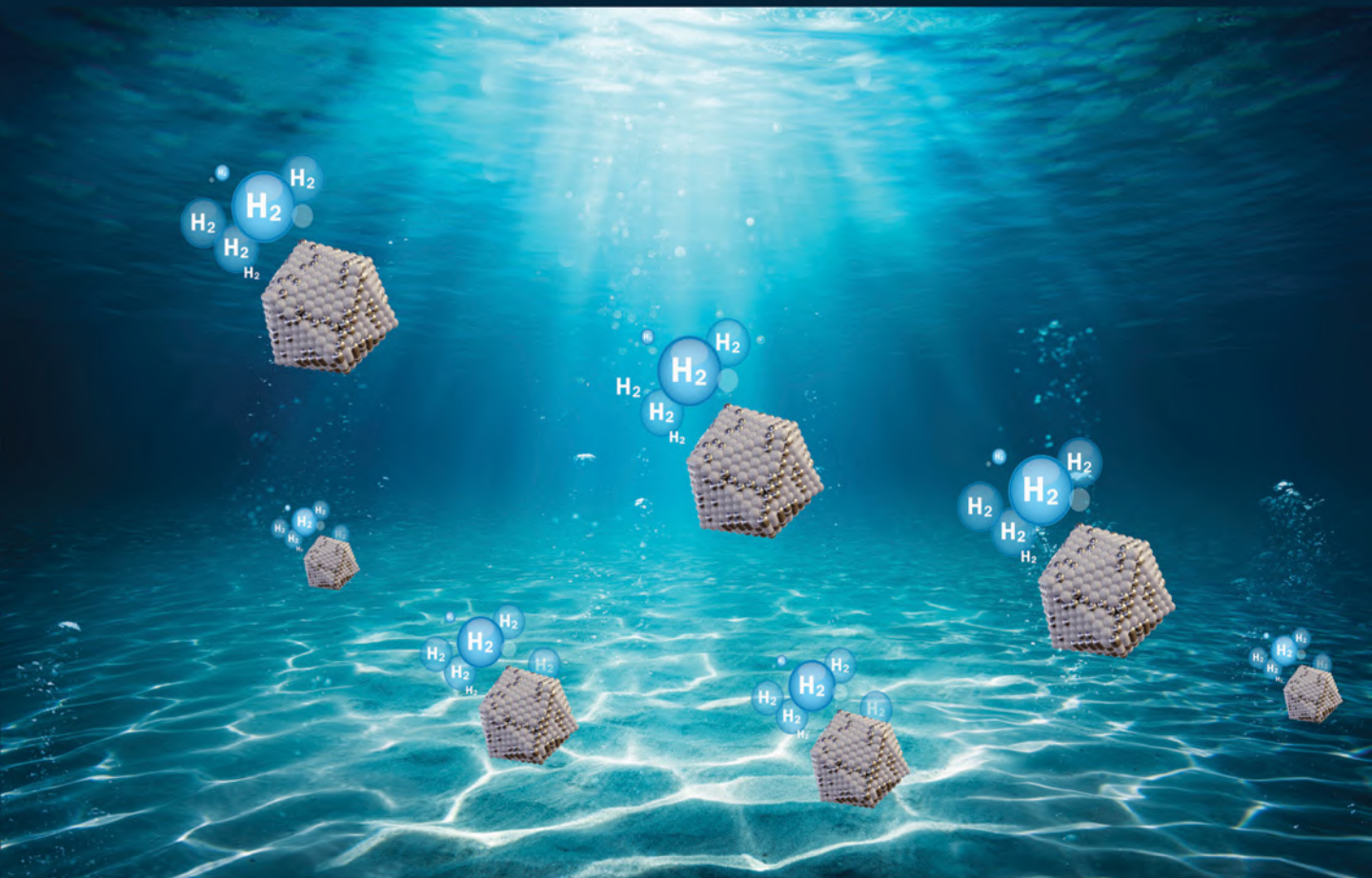


Photochemical Splitting of Water

Fundamentals to Applications



Edited by
Soney C. George
Luís P. M. Santos
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PHOTOCHEMICAL SPLITTING OF WATER

Fundamentals to Applications

Edited by

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Contents

List of contributors ix

Preface xiii

1. Potential of water splitting in the global energy future

Sajith Kurian, Luis P.M. Santos and Soney C. George

- 1.1 Introduction—global energy challenge 1
 - 1.2 Hydrogen economy 3
 - 1.3 Water: the potential source of hydrogen 6
 - 1.4 Role of artificial intelligence and additive manufacturing in water electrolysis 14
 - 1.5 Future prospects 16
 - 1.6 Conclusion 17
- References 17

2. Concepts, kinetics, and mechanism of water splitting

Rohit Gupta and Rahul Gupta

- 2.1 Introduction 23
 - 2.2 Kinetics of splitting water techniques 27
 - 2.3 Comparison of the mechanisms of splitting water by electrolysis method and photochemical water splitting 38
 - 2.4 Case study 38
 - 2.5 Learning and knowledge outcomes 45
 - 2.6 Conclusion 46
- References 47

3. Technologies for water splitting

Rakhi Khandelwal

- 3.1 Introduction 51
- 3.2 Water-splitting technologies 52
- 3.3 Challenges of water-splitting technologies 63
- 3.4 Comparative study of various water-splitting technologies 65

- 3.5 Future aspects of water-splitting technologies 65
 - 3.6 Case study: Seawater to Green Hydrogen: A Prototype by IIT Madras Scientists 67
 - 3.7 Conclusion 71
- References 71
- Further reading 73

4. Instrumentation and experimental setup for photochemical splitting of water

R. Anjana, Nithya S. George, Ayona K. Jose, Jibi Kunjumon, P.A. Aleena and D. Sajan

- 4.1 Introduction 75
 - 4.2 Cell design 78
 - 4.3 Electrode considerations 83
 - 4.4 Cell setup in a photochemical water-splitting reaction 86
 - 4.5 j–V (photocurrent) analysis 91
 - 4.6 Determination of flat band potential (E_{fb}) 92
 - 4.7 Two-electrode j–V measurement 92
 - 4.8 Conclusion 93
- References 93

5. Photocatalytic water splitting

Shalini Viswanathan, A.C. Swathi and K. Aparna

- 5.1 Introduction 97
 - 5.2 Material design for photocatalytic water splitting 100
 - 5.3 Reaction setup of water-splitting devices 106
 - 5.4 Recent progress in photocatalytic water splitting 108
 - 5.5 Case study 110
 - 5.6 Constraints in photocatalytic water splitting 112
 - 5.7 Conclusions 112
- References 114

6. Photoelectrochemical water splitting
Seema Rani, Soumyadip Sharangi, Subhabrata Das,
Mansi Pahuja and Kaushik Ghosh
- 6.1 Introduction 119
6.2 Photoelectrochemical water splitting: working principles 120
6.3 Materials for photoelectrochemical water splitting 126
6.4 Role of electrolyte 130
6.5 Advancements in photoelectrochemical water splitting 133
6.6 Case Study 136
6.6 Conclusion 139
6.7 Future outlook 139
References 140
7. Selection of materials and cell design components for photochemical splitting of water
Sapna Balayan, Mamta Shandilya, Itika Kainthla and Gun Anit Kaur
- 7.1 Introduction 143
7.2 Background of water-splitting 145
7.3 Material selection for photochemical splitting of water 151
7.4 Cell Design 155
7.5 Future perspective and recommendations 157
7.6 Conclusion 158
References 159
8. Noble metal-based catalysts for water splitting
Lekshmi Krishna, Paulose Thomas, Angel Susan Cherian and Anju K. Nair
- 8.1 Introduction 163
8.2 Fundamentals of water splitting 165
8.3 Catalysis in water splitting 166
8.4 Noble metals: properties and characteristics 168
8.5 Noble metals in hydrogen evolution reaction 171
8.6 Noble metal-based photocatalysts 179
8.7 Noble metal-free alternatives 181
8.8 Comparative analysis of noble metals versus noble metal-free catalysts 182
- 8.9 Challenges and limitations 184
8.10 Recent trends and future directions 186
8.11 Future prospects for noble metals in water-splitting technologies 187
8.12 Conclusion 188
References 189
9. Noble metal-free catalysts – oxides, chalcogenides, nitrides, oxynitrides for water splitting
Swapnali Walake, Pragati Thakur and Yogesh Jadhav
- 9.1 Introduction 193
9.2 Electrochemical and photo-electrochemical water splitting 194
9.3 Photocatalytic water splitting 196
9.4 Transition metal oxides, chalcogenides, nitrides, oxynitrides catalysts 197
9.5 Mechanism of water splitting 197
9.6 Strategies to improve water splitting 206
9.7 Conclusion and future prospects 212
References 213
10. Metal ion incorporated metal oxides for water splitting
Anju John, Jain Maria Thomas and Jesty Thomas
- 10.1 Introduction 217
10.2 Mechanism of metal oxide–assisted photochemical water splitting 219
10.3 TiO₂-based photocatalysts 221
10.4 ZnO-based photocatalysts 226
10.5 WO₃-based photocatalysts 229
10.6 Case studies 232
10.7 Conclusion and future perspective 237
References 237
11. Plasmonic material and quantum dot sensitized photocatalysts for water splitting
Nikita Chaudhary, Jyoti Jyoti and Kaushik Ghosh
- 11.1 Introduction 243
11.2 Plasmonic materials for PEC 244
11.3 Surface plasmon resonance 244
11.4 Design 250
11.5 PEC system based on quantum dots 250
11.6 Photoanode based on quantum dots 251

- 11.7 Surface customization of quantum dots 256
11.8 Photocathode based on quantum dot 257
11.9 Quantum dots assembly 258
11.10 Tandem quantum dot-based PEC architecture 259
11.11 Case study for TiO₂-based photoanode 260
11.12 Conclusion 260
References 262
12. Carbon-based materials for water-splitting
Mansi Pahuja, Mohd Afshan, Daya Rani, E.M. Harini and Kaushik Ghosh
- 12.1 Introduction 269
12.2 Carbon nanomaterials 270
12.3 Case study 286
References 290
13. Metal organic frameworks water splitting
Olugbenga Akande and Jude. A. Okolie
- 13.1 Introduction 295
13.2 Overview of different metal organic frameworks used in water splitting 296
13.3 Advances in metal-organic framework photocatalysts for efficient water-splitting 298
13.4 Types of water-splitting methods for extraction of heavy metals 307
13.5 Extraction of heavy metals using hydrogen evolution reaction 309
13.6 Analyzing chemical bonding via raman spectroscopy 310
13.7 Case study 310
13.8 Conclusion 313
References 313
14. 2D materials for water splitting
Misbah Mirza, Muhammad Safdar, Nazia Yasmin and Sadia Yasmin
- 14.1 Introduction 319
14.2 2D materials 321
14.3 2D materials superiority 323
14.4 Synthesis techniques of 2D materials 325
14.5 Characterization techniques for 2D materials 326
- 14.6 Mechanism of water splitting 329
14.7 2D materials for water splitting 333
14.8 SACs supported on diverse 2D materials 341
14.9 Conclusions 348
References 349
15. Conjugated polymer materials for water-splitting
Benjamin Tawiah, Emmanuel A. Ofori, Yang Ming and Bin Fei
- 15.1 Introduction 361
15.2 The basics of water-splitting 363
15.3 CP material synthesis and characterization 368
15.4 Photocatalytic water-splitting with CPs 379
15.5 Challenges and future perspectives 383
15.6 Case study: practical application of CP for water-splitting 385
15.7 Conclusion 387
References 387
16. Role of cocatalyst in water splitting
Sumesh George and Jain Maria Thomas
- 16.1 Introduction 395
16.2 Approaches to enhance the photocatalytic activity 397
16.3 Significance of cocatalysts in water splitting 398
16.4 Factors influencing the performance of cocatalyst 399
16.5 Types of cocatalysts 399
16.6 Conclusion and future perspective 417
References 418
17. Nanostructured materials for water-splitting
Suman Thakur and Sharda Bharti
- 17.1 Introduction 427
17.2 Conventional catalysts 429
17.3 Synthesis and properties of nanostructured materials 431
17.4 Metal-based nanostructured materials for water-splitting 437
17.5 2D materials and heterostructures 440

17.6 Nanostructured materials for photoelectrochemical water-splitting	442	18.7 Case study	471
17.7 Commercial prospects and technological challenges	446	18.8 Conclusion	482
17.8 Case study on nanostructured materials for water-splitting	446	References	482
17.9 Conclusion and future perspectives	450		
References	451		
		19. Challenges for photoelectrochemical water-splitting technology for the near-future	
		Gawel Sołowski and Fethi Ahmet Özdemir	
18. Photovoltaic electrochemical integration for water-splitting		19.1 Introduction	487
Princemon Philip, Ajesh K. Zachariah and Anju K. Nair		19.2 Methodology	488
18.1 Introduction	457	19.3 Discussion	489
18.2 Water-splitting	459	19.4 Learning, knowledge outcomes, and conclusions	499
18.3 Photovoltaic systems for water-splitting	462	References	499
18.4 Electrochemical systems for water-splitting	465		
18.5 Efficiency of water-splitting	469	Index	507
18.6 Photovoltaic electrocatalysis	470		

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Preface

Splitting of water is an area of active research for the last few decades. This research field is remarkably improved day by day as the researchers are focused on developing photocatalysts based on nanomaterials to enhance the efficiency of water splitting. Nanostructured materials and nanocomposites based on noble and non-noble metals, semiconductors, transition metal oxides, MOF, 2D materials, conjugated polymers, quantum dots, and carbonaceous materials have shown promise in improving light absorption and enhancing electron transfer processes. Some new designs such as tandem photoelectrochemical cells where two or more photocatalysts are stacked together to capture a broader spectrum of light, increasing overall efficiency, are also in progress. The photochemical water splitting technique contains great potential for clean hydrogen production although several challenges are there. Low efficiency is one of the most important challenges and researchers are concentrating on developing extraordinary catalysts that raise efficiency several times higher than the currently available ones.

Many efficient photocatalysts are made from rare or expensive materials, which raise the cost of large-scale hydrogen production. Long-term stability of the photocatalysts under operating conditions is another major challenge. Many materials degrade over time when exposed to light and water. Harnessing the full spectrum of sunlight and optimizing the absorption of visible light (instead of just UV light) is a key area of research. While significant

challenges remain in terms of efficiency, cost, and stability, ongoing research into new materials, better catalyst design, and improved systems could make this process a viable technology for sustainable hydrogen production in the future.

The advancement of research in the field of splitting water is discussed in this book. Chapter 1 provides the potential of water splitting in the global energy future. Chapter 2 focuses on the concepts, kinetics, and mechanism of water splitting. Chapter 3 discusses the technologies adopted for water splitting and Chapter 4 guides us to instrumentation and experimental setup for photochemical splitting of water. Various aspects of photocatalytic water splitting are discussed in Chapter 5. Chapter 6 discusses photoelectrochemical water splitting whereas the selection of materials and cell design is described in Chapter 7. Chapter 8 narrates on noble metal-based catalysts and Chapter 9 on noble metal-free catalysts, including oxides, chalcogenides, nitrides, and oxynitrides for water splitting. Chapter 10 illustrates the metal ion incorporated metal oxides for water splitting. Plasmonic material and quantum dots sensitized photocatalysts for water splitting are discussed in Chapter 11 and Chapter 12 brings us to a tour of carbon-based materials for water splitting. MOF-assisted water splitting is narrated in Chapter 13 and in Chapter 14, 2D materials for water splitting are concentrated. Chapter 15 leads us into a deep discussion on conjugated polymer materials for water splitting. Chapter 16 discusses the role of cocatalyst in water

splitting, and Chapter 17 on nanostructured materials for water splitting. Chapter 18 throws a light on photovoltaic electrochemical integration for water splitting and Chapter 19 concludes with challenges for photoelectrochemical water splitting technology for the near future.

The immense contributions of all authors to the book are admired. The reviewers who reviewed the chapters within the agreed time and gave valuable suggestions are recognized with appreciation. We are deeply grateful to the editorial team members of Elsevier Publishers for their

guidance and sustained support in this venture. We are profoundly indebted to the support, guidance, and motivation of our management, colleagues, and family members. I hope that this book gives a delightful experience to the readers who focus on water splitting-related research.

Editors

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Photovoltaic electrochemical integration for water-splitting

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18.1 Introduction

The world's energy supply is largely dependent on finite resources such as petroleum, coal, and natural gas. In recent decades, rising public concern over the challenges linked to fossil fuel usage and the large-scale CO₂ emissions as a greenhouse gas has spurred the demand for innovative energy conversion methods that utilize green and renewable sources (Vesborg and Jaramillo, 2012; Perera, 2017; Lewis and Nocera, 2006; Armaroli and Balzani, 2007). Solar energy is the sole renewable resource capable of replacing fossil fuels and addressing the rising environmental needs (Asif and Muneer, 2007; Lewis and Nocera, 2006). Even though solar energy can be harnessed to generate electricity with the most frequently utilized solar panels [or photovoltaic (PV) cells, abbreviated as PV], the intermittent nature of solar energy due to natural cycles poses a significant challenge to a sustainable energy supply. To address this issue, many researchers are working on converting solar energy into chemical compounds that can be generated when the sun shines and stored for use on demand (Yin et al., 2020).

The most promising method to utilize solar energy is using it to produce hydrogen through photocatalytic water-splitting. Currently, over 95% of H₂ gas is produced from fossil fuels, leading to significant environmental concerns (Bak et al., 2002a). As an alternative, water-splitting powered by solar energy can generate high-purity, eco-friendly hydrogen (Bak et al., 2002b). This method is considered a green and sustainable technology that can support the hydrogen economy (Momirlan & Veziroglu, 2005). Hydrogen is the purest energy source, useful for powering eco-friendly vehicles, fuel cells, home heating, and airplanes (Dorner et al., 2010). Additionally, using hydrogen for energy storage and transfer offers a long-term strategy to reduce global CO₂ emissions by converting CO₂ into valuable hydrocarbons (Jessop et al., 1995; Ashley et al., 2009).

In theory, PV-electrolysis systems could achieve 90%–95% of the efficiency of PV cells, resulting in approximately 57% efficiency for a 3-junction cell and around 62% for a 4- or 5-junction cell. These figures suggest there is considerable potential for enhancing the performance of PV-electrolysis system prototypes. In photoelectrochemical (solar) water-splitting devices, PEC cells typically include at least one light-absorbing electrode, which is usually a single semiconductor or a combination of two semiconductors in a heterojunction. PEC tandem cells, however, feature dual light absorbers, either connected by wires or operating wirelessly, and utilize the photovoltage generated by both photoelectrodes (Walter, 2010; Chen, 2019; Nam, 2018; Zeng, 2017; Bai, 2016). Fig. 18.1 illustrates a sustainable strategy for advancing the hydrogen economy by integrating renewable energy sources with electrochemical water-splitting (Zhang et al., 2020).

In this book chapter, we offer a comprehensive overview of the principles underlying the integration of PV systems with electrochemical cells for water-splitting. We also discuss the significance and potential of this integration in the context of renewable energy production and sustainable hydrogen generation. Additionally, we explore the mechanisms involved in water-splitting using integrated PV-electrochemical systems and examine the materials used for PV cells and electrochemical catalysts, with a focus on their efficiency, stability, and cost-effectiveness.

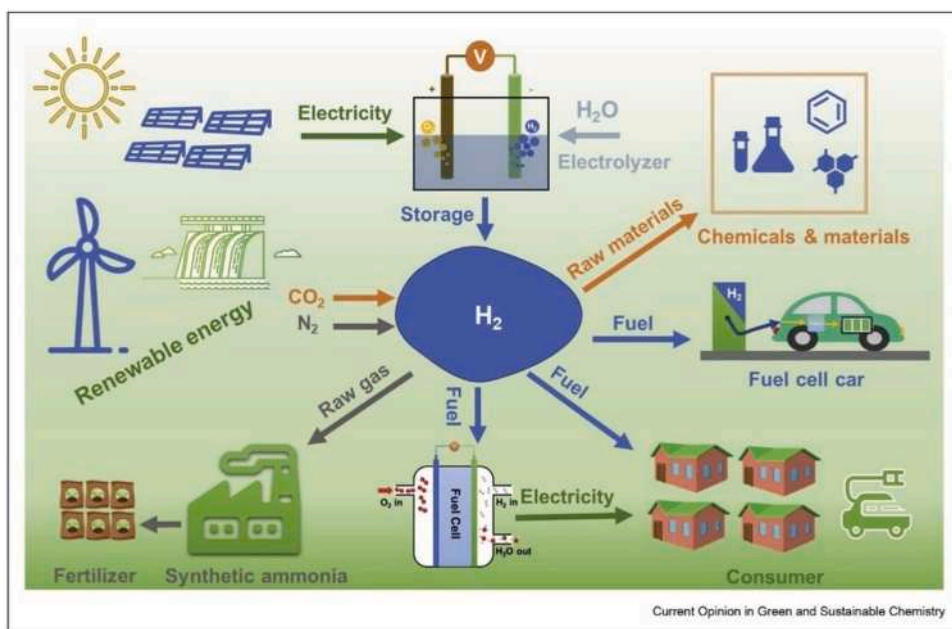


FIGURE 18.1 A sustainable approach to supporting the hydrogen economy involves integrating renewable energy sources with electrochemical water-splitting. (Zhang et al., 2020). Source: Copyright reserved to the Wiley (Creative Commons Attribution 4.0 Unported License).

18.2 Water-splitting

From a thermodynamic perspective, splitting water is an uphill process that does not occur spontaneously and necessitates external energy to proceed, as the reverse reaction happens readily. Fig. 18.2 summarizes various water-splitting methods. These include thermolysis (e.g., thermochemical cycles), electrolysis (e.g., electrocatalysis), photolysis (e.g., photocatalysis), and biolysis (e.g., dark fermentation). Hydrogen production can also be achieved using a combination of energy forms. Key hybrid energy systems include thermal + electrical (e.g., thermoelectrolysis, high-temperature electrolysis), electrical + photonic (e.g., photoelectrolysis, PV electrolysis), and photonic + biochemical (e.g., biophotolysis, photofermentation). Hybrid systems are typically more thermodynamically advantageous than nonhybrid systems because they incorporate cheaper or renewable resources for part of the required energy, which lowers overall operational costs, reduces activation barriers, improves the speed of chemical reactions and increases the rate of hydrogen production.

18.2.1 Basics of water-splitting

The overall process of water electrolysis consists of two half-cell reactions: the water reduction reaction (hydrogen evolution reaction [HER]) and the water oxidation reaction (oxygen evolution reaction [OER]). The cathodic (HER: Eqs. 18.1 and 18.3) and anodic (OER: Eqs. 18.2 and 18.4) reactions vary depending on the electrolyte conditions (pH of the solution) and can be represented as follows, with standard hydrogen electrode (SHE) indicating the standard hydrogen electrode (Spöri et al., 2017, Mahmood et al., 2018)

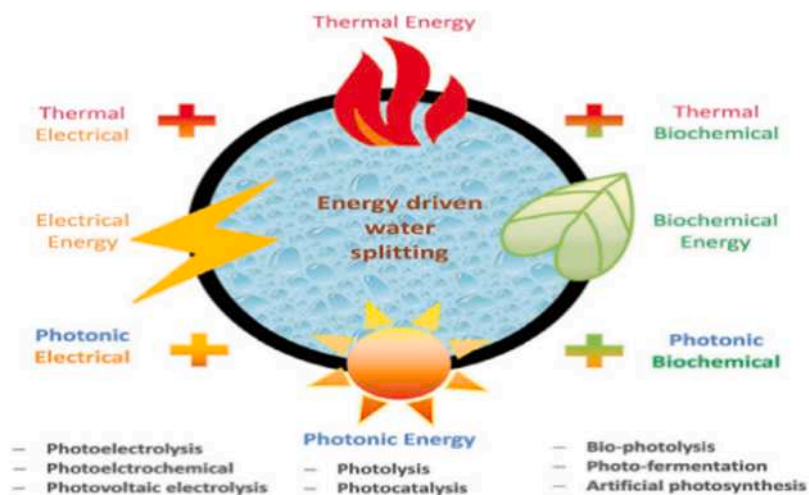
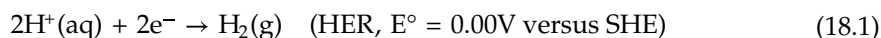


FIGURE 18.2 Various energy driven water-splitting routes by using thermal, electrical, biochemical and photonic energy or their combinations (Si et al., 2017). Source: Copyright reserved to the Wiley (Creative Commons Attribution 4.0 Unported License).

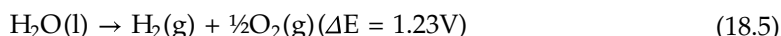
In acidic condition (pH 0),



In alkaline conditions (pH 14),



Overall reaction can be written as,

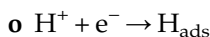


The water-splitting reaction is a thermodynamical uphill process, requiring a net Gibbs free energy input of 237 kJ/mol.

The Volmer-Tafel and Volmer-Heyrovsky pathways describe different mechanisms of the HER (Shinagawa et al., 2015). These pathways detail the steps involved in reducing protons to produce hydrogen gas (H_2) on an electrode surface. Let's break down each pathway:

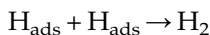
18.2.2 Volmer-Tafel pathway

18.2.2.1 Volmer step (electrochemical adsorption)



- o A proton from the electrolyte gains an electron from the electrode and adsorbs onto the electrode surface as a hydrogen atom (H_{ads}).

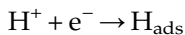
18.2.2.2 Tafel step (chemical desorption)



Two adsorbed hydrogen atoms combine to form a hydrogen molecule, which then desorbs from the electrode surface into the electrolyte or gas phase.

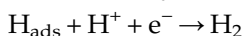
18.2.3 Volmer-Heyrovsky pathway

18.2.3.1 Volmer step (electrochemical adsorption)



A proton from the electrolyte gains an electron from the electrode and adsorbs onto the electrode surface as a hydrogen atom (H_{ads}).

18.2.3.2 Heyrovsky step (electrochemical desorption)



An adsorbed hydrogen atom reacts with another proton (H^+) from the electrolyte and gains an electron to form a hydrogen molecule (H_2), which then desorbs from the electrode surface.

In an alkaline electrolyte, the HER begins with the reduction of a water molecule at the active site of the catalysts. This process forms a proton at the active site. Consequently, more energy (or overpotential) is typically needed compared to acidic media to generate protons by breaking down water molecules. Unlike the HER, the OER requires a four-electron transfer process to produce 1 mole of oxygen gas (O₂), making it a bottleneck in the entire water electrolysis system. Although four different reaction mechanisms for the OER have been proposed (Matsumoto and Sato 1986).

18.2.4 Electrochemical oxide pathway

This pathway involves the formation and involvement of higher oxidation state intermediates through direct electrochemical steps.

18.2.4.1 Formation of metal-OH (M-OH)



A water molecule adsorbs onto the catalyst (M), forming a hydroxyl group (M-OH) with the release of a proton and an electron.

18.2.4.2 Formation of metal-O (M-O)



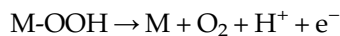
The M-OH undergoes further oxidation to form an oxo group (M-O), releasing another proton and electron.

18.2.4.3 Formation of metal-OOH (M-OOH)



The M-O reacts with another water molecule to form a hydroperoxo group (M-OOH), with the release of a proton and an electron.

18.2.4.4 Formation of oxygen gas

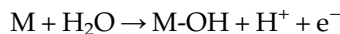


The M-OOH is further oxidized, releasing O₂ and regenerating the catalyst site, with the release of a proton and an electron.

18.2.5 Oxide pathway

The oxide pathway involves the formation of bulk or surface oxides, which then participate in the OER process.

18.2.5.1 Formation of metal hydroxide



A water molecule adsorbs onto the metal surface, forming a MOH, releasing a proton and an electron.

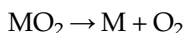
18.2.5.2 Formation of metal oxide and water release

- o $\text{MOH} \rightarrow \text{MO} + \text{H}_2\text{O}$
- o The metal hydroxide (MOH) loses a water molecule, forming a metal oxide (MO).

18.2.5.3 Formation of higher oxidation state oxide

- o $\text{MO} + \text{H}_2\text{O} \rightarrow \text{MO}_2 + 2 \text{H}^+ + 2\text{e}^-$
- o The MO is further oxidized by another water molecule, forming a higher oxidation state oxide (MO_2), releasing protons and electrons.

18.2.6 Oxygen evolution



The higher MO_2 decomposes, releasing O_2 and regenerating the catalyst surface.

In the OER mechanism in alkaline media, the initial step involves the adsorption of a hydroxide ion on the catalyst's active site. Subsequently, the evolution of O_2 can proceed via either a radical oxo coupling pathway or a superoxo intermediate pathway (Song et al., 2018). Fig. 18.3 depicts the mechanism of electrochemical water-splitting reactions in an acidic aqueous solution (Minoh et al., 2022).

18.3 Photovoltaic systems for water-splitting

18.3.1 Basic principle of the photovoltaic system

When light hits a photovoltaic PV cell, it converts the energy into electricity. The word "photovoltaic" is derived from "photo," which refers to light, and "voltaic," which pertains to electricity. When the cell is illuminated, it captures photons from the sunlight, which excites electrons and causes them to move away from their atoms, creating holes. When the PV cell is linked to a load, the voltage difference causes charges to shift from the n-side to the p-side of the cell, resulting in electricity generation.

Generally, a single PV cell generates approximately 0.5 V, while the amount of current produced depends on factors such as weather conditions, sunlight intensity, and the cell's surface area (Ahmad et al., 2023, Jiang et al., 2017, Chan et al., 2016). To improve the performance of PV cells, they are usually designed into larger modules or panels with cells connected in series or parallel arrangements. Different configurations provide different enhancements; series connections increase voltage, while parallel connections boost current. For certain applications, PV cells can be arranged in a hybrid configuration to create a PV array customized to fulfill specific requirements.

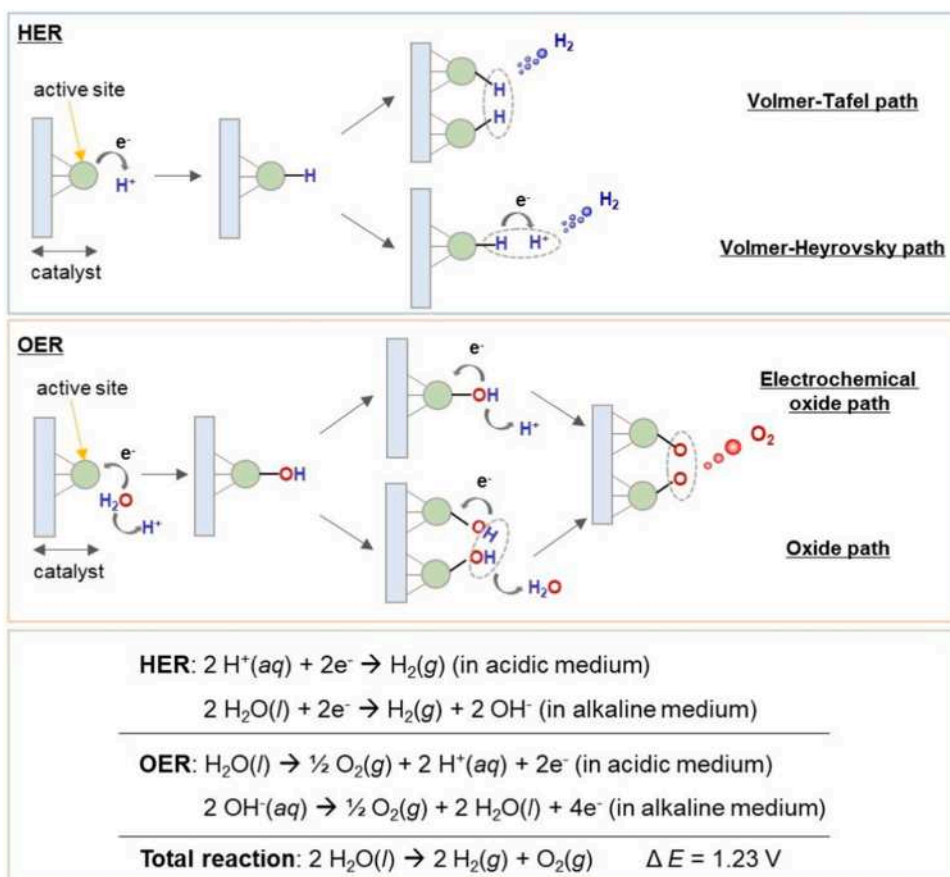


FIGURE 18.3 Mechanism of electrochemical water-splitting reactions in an acidic aqueous solution. (Minoh et al., 2022). Source: Copyright reserved to the Chemistry Europe (Creative Commons Attribution 4.0 Unported License).

18.3.2 Types of solar photovoltaic technology

Solar PV technology has captured considerable attention within communities and society, establishing itself as one of the leading renewable energy sources. Currently, three generations of solar PV technologies have been developed, as illustrated in Fig. 18.4 (Samsudin, 2023).

18.3.3 First generation: traditional silicon-based solar cells

The initial generation of solar PV technology is mainly composed of crystalline silicon solar cells, available in both monocrystalline and polycrystalline forms. These cells have led the market for many years, thanks to their high-efficiency and dependable performance. Monocrystalline silicon cells are known for their high-efficiency, typically ranging between 15% and 20% in commercial products, with laboratory efficiencies reaching around 26%–27% (Allouhi et al., 2022; Samsudin et al., 2020). Polycrystalline silicon cells, while slightly less efficient, offer a more cost-

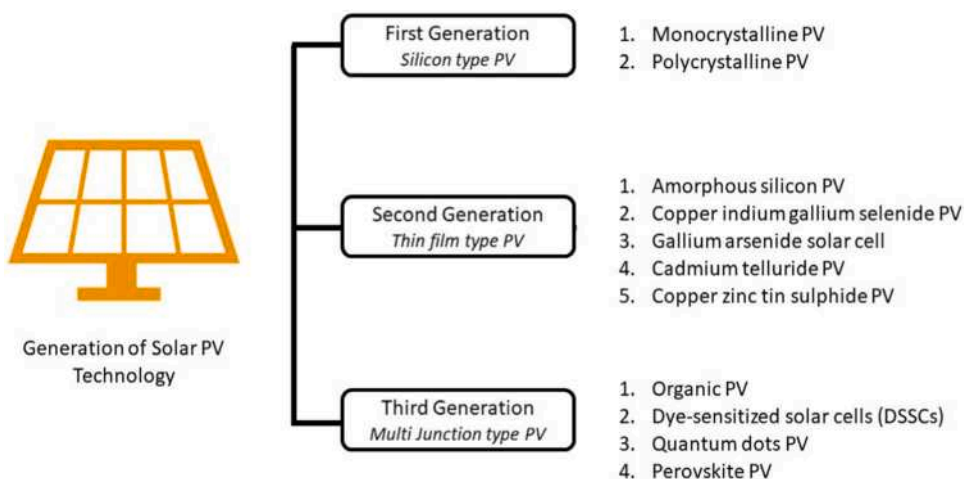


FIGURE 18.4 Generations of solar PV technologies that has been developed (Samsudin, 2023). Source: Copyright reserved to the energies (Creative Commons Attribution 4.0 Unported License).

effective alternative. Monocrystalline silicon PV technology utilizes PV cells composed of a single silicon crystal derived from sand. The manufacturing of these cells involves a complicated, multistage process that includes extracting, purifying, and heating silicon to elevated temperatures, followed by the use of the Czochralski method (Saga, 2010). Due to the high manufacturing costs associated with monocrystalline PV systems, polycrystalline silicon PV technology has been developed as a more cost-effective alternative (Allouhi et al., 2022; Saga, 2010). While both technologies operate on the same basic principles, polycrystalline PV systems differ slightly in their crystalline silicon structure. In polycrystalline systems, the silicon consists of multiple crystal grains, which introduce additional recombination sources that affect the total efficiency of the PV cells. Polycrystalline PV technology generally attains efficiencies between 15% and 20%, varying based on the particular technology implemented and the environmental circumstances in which the system functions (Kenu, 2020; Pastuszak and Wegierek, 2022).

18.3.4 Second generation: thin-film solar cells

The next generation of solar PV technology brought forth thin-film solar cells, created to minimize material consumption and lower production costs. These cells are made up of single or multiple layers of PV elements. This generation includes various PV systems such as amorphous silicon, copper indium gallium selenide, gallium arsenide (GaAs), cadmium telluride, and copper zinc tin sulfide (Huang and Wang, 2018; Radue and van Dyk, 2010; Mateo et al., 2022). Among these, amorphous silicon PV is the most advanced thin-film option, featuring a p-i-n or n-i-p junction configuration that creates an internal electric field and offers a superior absorption capacity of 1.1–1.7 eV, surpassing the first generation's 1.1 eV (Mikolasek et al., 2019). However, its low structural homogeneity affects electron and hole movement, impacting absorption. To address this, researchers have developed heterojunctions of amorphous and crystalline silicon (heterojunction technology [HJT] cells), which improve efficiency, open-circuit voltage, and thermal stability (Zeng et al., 2023).

GaAs and CdTe PV systems are also notable in this generation. GaAs is preferred for space applications due to its radiation resistance. CdTe, with an energy gap of 1.4 eV, can capture a broad spectrum of light intensities and has seen efficiency improvements from over 10% in the early 1980s to more than 15% in recent years (Bonnet, 2012).

18.3.5 Third generation: emerging and advanced photovoltaic technologies

Third-generation solar PV technology represents a significant leap in solar energy conversion, aiming to address the shortcomings of previous generations and attain high-efficiency while keeping production costs low. This generation includes innovative approaches such as dye-sensitized solar cells (DSSCs), organic photovoltaics (OPVs), perovskite solar cells, quantum dot solar cells, and tandem solar cells, among others. DSSCs use organic dye molecules to capture sunlight and produce electrons. They are recognized for their affordable production costs and their effectiveness in low-light environments. The architecture typically includes a photosensitizer (dye), a semiconductor (usually titanium dioxide), and a liquid electrolyte. OPVs use organic molecules or polymers to transform solar energy into electrical power. They provide benefits including mechanical flexibility, light weight, and the possibility of cost-effective production via roll-to-roll manufacturing. Recent progress in materials and device engineering has notably enhanced the power conversion efficiency of OPV cells. Perovskite solar cells have attracted considerable interest because of their excellent efficiency and relatively straightforward manufacturing process. These cells employ a perovskite-structured material as the layer responsible for capturing light. These cells use a perovskite-structured compound as the light-harvesting active layer. They have rapidly increased in efficiency, reaching over 25% in laboratory settings, making them one of the most promising emerging PV technologies. Quantum dot solar cells incorporate nanoscale semiconductor materials (quantum dots) that have unique electronic properties due to quantum mechanics. These cells can be designed to capture various segments of the solar spectrum by adjusting the size of the quantum dots, potentially leading to higher efficiencies (Solak and Irmak, 2023; Alami et al., 2022).

18.4 Electrochemical systems for water-splitting

Electrochemical water-splitting, which produces hydrogen of high-purity with no CO₂ emissions, holds great promise for achieving a sustainable energy future (Seh et al., 2017; Grigoriev et al., 2020). In contrast to coal gasification and steam-methane reforming, electrochemical water-splitting has benefits owing to the abundant availability of basic inputs like electricity and water (Kou et al., 2021).

18.4.1 Overview of electrolyzers

Various types of water electrolyzers, such as Proton Exchange Membrane (PEM), alkaline, Anion Exchange Membrane (AEM), and Solid Oxide electrolyzers, are defined based on their operating temperatures and the electrolytes employed (Li and Baek, 2021; Sapountzi

et al., 2017; Zakaria and Kamarudin, 2021). Solid oxide electrolyzers operate at elevated temperatures (700°C–800°C), whereas the other three operate at much lower temperatures (typically below 100°C). Despite having a theoretical efficiency of up to 100%, solid oxide electrolyzers face challenges due to high operating temperatures causing safety and durability issues (Sapountzi et al., 2017). In PEM, alkaline, and AEM water electrolyzers, two electrodes are submerged in a water-based electrolyte and linked to an external circuit. This setup facilitates the OER at the anode and the HER at the cathode (Zakaria and Kamarudin, 2021; Lagadec and Grimaud, 2020).

Alkaline water electrolyzers employ an alkaline electrolyte, that is, constantly circulated through the electrolysis stack, where it generates hydrogen and oxygen gases. They have several advantages, such as fast start-up, high-purity hydrogen production, compact design, and low resistance losses. The primary element is the diaphragm, which facilitates ion movement between the anode and cathode. Additionally, heat exchangers are employed to ensure the electrolyte remains at the ideal temperature.

PEM water electrolyzers involve a membrane electrode assembly containing catalysts and the PEM. The ionomer within the system manages liquid or gas flow, ensures ionic conductivity, and provides mechanical stability for the catalysts (Chen et al., 2022).

AEM water electrolyzers are recognized as a technology of the third generation, combine features of both alkaline and PEM electrolyzers. They use transition-metal-based materials and a solid polymer electrolyte structure. While alkaline electrolyzers use concentrated KOH/NaOH solutions, AEM electrolyzers can use distilled water or low-concentration alkaline solutions (Hassan et al., 2022). AEM electrolyzers with hydrocarbon AEM and low-cost electrodes are promising for hydrogen production but need further research on applicable catalysts and designs.

The efficiency and yield of water electrolyzers depend on the selection and design of membranes, support materials, binders/ionomers, gas diffusion, operational conditions, local pH values, and impurities (Table 18.1).

18.4.2 Catalysts for hydrogen and oxygen evolution reactions

18.4.2.1 Hydrogen evolution reaction electrocatalysts

HER electrocatalysts generally fall into two principal types: those that use noble-metals and those that employ nonnoble metals.

18.4.2.2 Noble-metal-based electrocatalysts

Noble metals, like those in the Pt group, exhibit excellent catalytic performance for HER. Nonetheless, their widespread use is restricted due to their rarity and high expense. To overcome this issue, it is essential to develop catalysts with minimal metal content and efficient metal use. Combining Pt with transition metals can greatly improve the efficiency of Pt usage and modify electronic environments, boosting HER electroactivity. In alkaline conditions, HER activity is typically reduced compared to acidic conditions because water dissociation on the Pt surface is less effective (Zhu et al., 2019). To improve this, Pt is often coupled with water dissociation promoters (Xie et al., 2019). Among various Pt-based electrocatalysts, regulating the metal composition on the surface is essential for improving

TABLE 18.1 Comparison of the main characteristics of alkaline, PEM and AEM water electrolyzers (Sun et al., 2023).

	Alkaline water electrolyzer	PEM water electrolyzer	AEM water electrolyzer
Separator	Diaphragm (Zirfon Perl 500 μm)	Nafion 117	AEM (20–100 μm)
Catalysts	Anode: Ni, Ni-Co alloys Cathode: Ni, Ni-Mo alloys	Anode: Ru/IrO ₂ Cathode: Pt, Pt-Pd	Anode: Ni, Fe, Co oxides Cathode: Ni and Ni alloys
Electrolyte	KOH (20–40 wt.%)	High-purity deionized water (18 M Ωcm)	Alkaline solution or deionized water
Ion transport	OH ⁻	H ⁺	OH ⁻
Temperature (°C)	50–80	50–80	50–70
Pressure (bar)	1–30	30–76	1–30
Current density (Acm ⁻²)	0.2–0.6	0.6–2.0	0.2–0.4
Cell voltage (V)	1.8–2.4	1.8–2.2	1.8–2.2
Efficiency (%)	60–70	70–80	–
Gas purity (vol%)	> 99.5	> 99.9999	> 99.99
Developing status	Mature technology	Mature for small scale	Under development
Advantages	Nonnoble metal catalysts, great durability, low capital cost	Compact design, fast response or start-up, high-purity production	Combined advantages of Alkaline and PEM water electrolyzers.
Disadvantages	Slow dynamics, corrosive electrolyte, further purification stage	Noble-metal catalysts, poor durability, high capital cost	Low OH ⁻ conductivity in polymeric membranes

PEM, Proton exchange membrane; AEM, anion exchange membrane.

electrocatalytic performance. Additionally, doping Pt-based materials with different metals improves catalytic performance while reducing Pt usage.

18.4.2.3 Nonnoble-metal-based electrocatalysts

Transition-metal carbides have garnered significant attention for developing nonnoble metal electrocatalysts. For instance, Mo₂C and WC demonstrate high catalytic activity for HER. In addition to their outstanding electrical conductivity, their hydrogen adsorption characteristics and d-band electronic density resemble those of Pt, which is believed to be a major factor in their high HER activity (Levy and Boudart, 1973; Kitchin et al., 2005; Vruble and Hu, 2012).

Research into transition-metal phosphides (TMPs) is progressing quickly in the creation of electrocatalysts that offer both high catalytic activity and stability in acidic and basic environments. The P atoms in TMPs are believed to play a crucial role because of their outstanding conductivity and distinctive electronic configuration. Since 2005, Ni₂P has been recognized as one of the most effective practical catalysts for HER (Liu and Rodriguez, 2005). Ni₂P exceeds the performance of bulk Pt and Ni due to the strong binding of hydrogen, produced during HER, to the hollow sites of the metal. This strong bonding increases the energy required for hydrogen to desorb from the surface of the metal. The inclusion of P atoms decreases the number of highly active Ni sites, resulting in a more moderate interaction with intermediates and products, a phenomenon known as the “ensemble effect” (Popczun et al., 2013). Nevertheless, the stability of the Ni₂P/Ti electrode, particularly in alkaline electrolytes, was inadequate. The NiCo₂P_x catalyst, on the other hand, shows exceptional longevity and consistent stability across different electrolytes, establishing it as a highly effective pH-universal catalyst for HER (Zhang et al., 2017).

Transition-metal chalcogenides (sulfides and selenides): In 2005, density functional theory (DFT) calculations conducted by Nørskov et al. demonstrated that the free energy of atomic hydrogen binding to the MoS₂ edge is similar to that of Pt. This finding underscores MoS₂'s potential as an effective electrocatalyst for HER (Hinnemann et al., 2005). To pinpoint the precise active site of MoS₂, Chorkendorf et al. synthesized triangular MoS₂ single crystals of various sizes on an Au(111) substrate. Their research revealed that HER activity is directly proportional to the number of edge sites on the MoS₂ catalyst, which are highly active for catalysis (Jaramillo et al., 2007). Building on this insight, several strategies, including nanostructure design and morphology optimization, have been proposed to enhance HER activity by exposing these active sites (Xie et al., 2013). In a different study, Jin et al. successfully prepared CoS₂ with tunable morphologies, including film, microwire, and nanowire (NW) forms. They systematically analyzed the structures, activities, and stabilities of these different morphologies, revealing that both activity and stability are enhanced depending on the morphology. Among the three types, CoS₂ NWs showed the greatest HER catalytic efficiency and stability, which is credited to their extensive effective electrode surface area and the effective removal of gas bubbles from the surface of the electrode (Faber et al., 2014). Additionally, doping with heteroatoms has been shown to be a successful approach for enhancing HER activity.

18.4.3 Oxygen evolution reaction electrocatalysts

OER electrocatalysts can be divided into two main categories: those derived from noble-metals and those derived from nonnoble metals.

18.4.3.1 Noble-metal-based electrocatalysts

Noble-metal and MO electrocatalysts, like RuO₂ and IrO₂, have traditionally been considered top materials for the OER due to their superior performance. However, their high cost and significant dissolution issues necessitate modifications to optimize their composition, structure, and morphology. Several approaches, such as heteroatom

doping and mixing with other transition metals, have been explored to enhance the activity, stability, and reduce costs (Su et al., 2018; Wang et al., 2019). Surface structure modifications, especially in creating hollow nanoparticles like nanocages and nano-frames, have been successful in boosting catalytic activity (Park et al., 2017). Other noble-metals like Rh, Au, Pt, and Pd are also being recognized as potential OER electrocatalysts. Designing bi- or tri-functional catalysts with these metals can improve performance for OER, oxygen reduction reaction, and HER. These catalysts are typically evaluated in alkaline solutions due to their lower dissolution resistance in acidic electrolytes. Controlling the morphology and composition is crucial for attaining the best electrocatalytic performance (Lu et al., 2016).

18.4.3.2 Nonnoble metal-based electrocatalysts

Nonnoble metal-based electrocatalysts have garnered significant research attention due to their low-cost and widespread availability. Attention has increasingly shifted towards identifying efficient noble-metal-free OER electrocatalysts. Zhang et al. (2016) developed a gelled FeCoW oxyhydroxide (W, Fe-doped CoOOH, G-FeCoW) with uniform metal distribution using the sol-gel method. This FeCoW oxyhydroxide exhibited an overpotential of 191 mV at a current density of 10 mA/cm² and demonstrated 500 hours of cycle stability, outperforming the benchmark Ni-Fe based catalyst (Zhang et al., 2016). Defect engineering is a useful approach for modifying the structural and electronic characteristics of electrocatalysts. Improving OER activity can be accomplished by adjusting the intermediate adsorption energy, which can occasionally lead to the discovery of unforeseen active sites (Xu et al., 2016). Beyond intrinsic changes for optimal intermediate species adsorption energy, the capacity to modify electron transport is crucial for enhancing OER activity (Lu et al., 2014; Zhou et al., 2018).

Most nonnoble metal catalysts are MOs and (oxy)hydroxides. Lately, a range of promising electrocatalysts, including TMPs, sulfides, and selenides, have exhibited remarkable catalytic performance for OER. Nonetheless, these compounds often show limited durability in highly oxidative environments within alkaline solutions. Therefore understanding the chemical nature of the true active sites has become a major focus in developing OER-related catalysts. Hu and colleagues synthesized nanostructured nickel iron diselenide (Ni_xFe_{1-x}Se₂) as a template precursor for in situ generation of a highly active nickel iron oxide catalyst. This catalyst demonstrated outstanding OER activity with an overpotential of only 195 mV at 10 mA cm² (Xu et al., 2016).

18.5 Efficiency of water-splitting

The efficiency of water-splitting, particularly through electrolysis, can vary depending on the specific method, the materials used for the electrodes, and the operating conditions. Table 18.2 estimates for the efficiency of different water-splitting technologies.

TABLE 18.2 Efficiency of different water-splitting technologies.

Sl. no.	Water-splitting process	Efficiency	Reference
1.	Alkaline water electrolysis	60%–80%	Ursua et al. (2012)
2.	Proton exchange membrane electrolysis	70%–85%.	Ayers et al. (2010)
3.	Solid oxide electrolysis cells	exceed 85% (above 800°C)	Graves et al. (2011)
4.	Photoelectrochemical (PEC) water-splitting	10%–20%,	Lewis and Nocera (2006)
5.	Thermochemical water-splitting	30%–40%.	Agrafiotis et al. (2015)

18.6 Photovoltaic electrocatalysis

Photo-electrochemical water-splitting (PEC) can be considered as an ideal method, because it is environmentally friendly and renewable in nature. This method efficiently transforms sunlight into chemical energy, enabling the oxidation or reduction of substances to produce valuable materials, including hydrogen ([Gopinath et al., 2022](#)).

Hydrogen fuel, which is environmentally friendly, storable, and renewable, can be effectively produced by splitting water, a resource, that is, abundantly available. However, the high voltage required for water electrolysis (>1.23 V) poses a challenge to cost-effectiveness. To address this, PEC cells are used to lower the voltage. When powered by solar-driven PV devices, PEC cells create an all-clean, efficient technology that relies solely on renewable sources, making this an area of significant research interest ([Chatterjee et al., 2022a,b](#)). Photovoltaic electrocatalysis (PV-EC) mitigates the limitations of both particulate photocatalysis and electrocatalysis. This method involves connecting the output of a PV module to an electrolyzer. Consequently, water-splitting occurs in a two-step process: (1) photon-to-electric conversion via the PV module and (2) electric-to-chemical energy conversion using electrolyzers with electrodes made from electrocatalytic materials. By employing PEMs between electrodes, H₂ and O₂ are generated separately.

In a study, Gimm et al. introduced an equivalent circuit model to evaluate the steady-state performance of photoelectrochemical cells. This model compares devices situated in various locations with differing average illumination levels and tilt angles. The findings indicate that using actual illumination data significantly affects the efficiency of PV-EC devices. The average annual solar-to-hydrogen (STH) efficiency is notably lower than the ideal value and is influenced by the tilt angle, with the optimal angle for latitudes similar to Europe's being approximately 40° ([Grimm et al., 2022](#)).

Landman and colleagues introduced a novel concept of cell separation within the PEC system, which decouples the PEC system into distinct oxygen and hydrogen cells. In this decoupled PEC setup, the researchers utilized the first generation of silicon PV modules to facilitate photoelectrocatalytic hydrogen production in a separate cell arrangement. The silicon PV module exhibited a short-circuit current of 164.5 mA and an open-circuit voltage of 5.4 V. Notably, charge carrier separation in both individual cells was achieved by incorporating battery-grade nickel hydroxide into each cell compartment ([Chatterjee et al., 2022a,b](#); [Lublow and Schedel-Niedrig, 2020](#)). Another work explores the use of perovskite/silicon tandem solar

cells integrated with a thermal exchanger, which significantly improves performance for scalable direct water-splitting. The study highlights the development of a modular approach to scale up the concept and discusses the stability and degradation mechanisms of these devices (Maragno et al., 2024). In other work, the efficiency of PV-assisted electrochemical water-splitting systems has been achieved using low-cost light-absorbing materials to attain high STH conversion rates. It demonstrates a PV-electrolysis system with an impressive STH efficiency, highlighting the potential for scalable hydrogen production (Jia et al., 2016). Finger et al. (2020) examine the use of silicon-based multijunction solar cells in integrated PV-EC systems, focusing on achieving high open-circuit voltages and efficient hydrogen production.

18.7 Case study

18.7.1 Title

Photovoltaic electrochemical integration for water-splitting.

18.7.2 Objective

The case study on “Photovoltaic electrochemical integration for water-splitting” typically aims to achieve the following objectives:

- 1. Efficiency improvement:** To enhance the efficiency of converting solar energy into chemical energy through water-splitting, leveraging the integration of PV and electrochemical systems.
- 2. Sustainable hydrogen production:** To develop a sustainable and clean method for producing hydrogen from water using solar energy, which can serve as a renewable energy source.
- 3. System integration:** To explore and optimize the integration of PV cells with electrochemical water-splitting processes, ensuring that the system operates efficiently and effectively.
- 4. Cost reduction:** To reduce the overall cost of hydrogen production by improving the performance and economic viability of the PV-electrochemical systems.
- 5. Technical feasibility:** To evaluate the technical feasibility of combining PV and electrochemical technologies, including the assessment of material compatibility, system design, and operational stability.

18.7.3 Scope

Project limitations

- 1. Limited time period:** Research projects often face constraints due to the academic calendar or funding timelines. This may affect the depth of experimentation and data collection.
- 2. Access to materials/tools:** Availability of specialized materials (like high-efficiency PV cells) and tools (such as advanced electrochemical testing equipment) can be a limiting factor.

- 3. Technical expertise:** The complexity of integrating PV systems with electrochemical water-splitting may require a high level of technical knowledge, which can be a constraint if the team lacks experience in certain areas.

Intended workflow (in brief)

- 1. Literature review:** Start with a comprehensive review of existing technologies and integration methods for PV water-splitting systems.
- 2. Design and simulation:** Develop theoretical models and simulations to predict the performance of different integration schemes.
- 3. Material selection:** Choose appropriate PV cells and electrochemical catalysts based on performance criteria.
- 4. System integration:** Construct the prototype by integrating the PV system with the electrochemical water-splitting setup.
- 5. Testing and optimization:** Conduct experiments to test the system's efficiency, stability, and scalability. Optimize parameters based on initial results.
- 6. Analysis and reporting:** Analyze the data, compare results with theoretical predictions, and prepare a comprehensive report.

Budget and costs

- 1. Materials:** Costs will vary based on the quality and quantity of PV cells, electrochemical catalysts, and other components.
- 2. Equipment:** Expenses for testing equipment, such as potentiostats or solar simulators, can be significant.
- 3. Labor:** Consider costs related to the team's time and expertise, including any hiring of additional staff or consultants.
- 4. Miscellaneous:** Budget for unexpected expenses, such as repairs, additional testing, or unforeseen challenges.

Planning carefully and addressing these factors will help in managing the project effectively and achieving meaningful results.

Audience

- 1. Researchers and scientists:**
 - **Who will find it useful:** Those working in the fields of renewable energy, materials science, and electrochemistry. Researchers focused on improving STH conversion efficiencies and developing sustainable energy solutions.
 - **Ability to follow:** They should have a strong background in PVs, semiconductor materials, and electrochemical processes. Familiarity with current challenges in water-splitting technology is essential.
- 2. Graduate and postgraduate students:**
 - **Who will find it useful:** Students pursuing degrees in energy systems, chemical engineering, or environmental science. Those interested in solar energy and hydrogen production would benefit from understanding the integration techniques discussed.
 - **Ability to follow:** They should have foundational knowledge in electrochemistry, renewable energy technologies, and an understanding of the principles behind water-splitting and PV systems.

3. Energy industry professionals:

- **Who will find it useful:** Engineers, technical consultants, and professionals involved in the development of renewable energy projects, particularly those focused on hydrogen production and solar energy integration.
- **Ability to follow:** Industry professionals with experience in PVs, electrochemical systems, and energy storage would be able to follow the case study, though they may require some background in the latest research developments.

4. Policy makers and environmental advocates:

- **Who will find it useful:** Those involved in developing policies for renewable energy adoption and sustainability goals. Advocates promoting clean energy solutions could use the case study to support policy changes or advocacy campaigns.
- **Ability to follow:** While not necessarily experts, they should have a general understanding of renewable energy technologies and the significance of hydrogen as a clean energy carrier.

5. Funding agencies and investors:

- **Who will find it useful:** Organizations and individuals interested in investing in cutting-edge renewable energy technologies or funding research in this area.
- **Ability to follow:** They would need a general understanding of the technology's potential, economic implications, and how it fits into the broader energy landscape.

Participants in the case study

- **Lead researchers:** Specialists in PVs and electrochemical processes who conducted the experimental work and analysis.
- **Collaborating institutions:** Universities, research centers, or companies specializing in renewable energy technologies.
- **Funding bodies:** Organizations that provided financial support for the research, including government agencies, private foundations, or industry partners.
- **Technical staff:** Engineers and laboratory technicians who supported the experimental setup and data collection.
- **Peer reviewers:** Academics and experts who reviewed the case study to ensure the validity and significance of the findings before publication.

18.7.4 Rationale

The case study on “PV Electrochemical Integration for Water-Splitting” addresses the critical need for sustainable energy solutions. The rationale for this activity is rooted in several key motivations:

1. **Energy crisis and environmental concerns:** The growing global demand for energy, coupled with the detrimental effects of fossil fuel consumption, has necessitated the exploration of renewable energy sources. Water-splitting, which produces hydrogen—a clean fuel—is seen as a promising solution. However, traditional methods of hydrogen production are energy-intensive and rely heavily on nonrenewable resources.
2. **Photovoltaic technology:** PV technology, which converts sunlight into electricity, offers a sustainable and abundant source of energy. By integrating PV with electrochemical

water-splitting, the aim is to harness solar energy to produce hydrogen efficiently. This integration could potentially lead to a self-sustaining, low-cost, and environmentally friendly method of hydrogen production.

- 3. Technological innovation:** The main issue being addressed is the inefficiency and cost associated with current hydrogen production methods. The experiment seeks to explore how effectively PV cells can be coupled with electrochemical systems to enhance the efficiency of water-splitting. The focus is on optimizing the materials, system design, and operational conditions to maximize hydrogen yield while minimizing energy loss.
- 4. Sustainable energy transition:** The experiment was held to contribute to the broader goal of transitioning to a hydrogen-based economy. By demonstrating the feasibility and scalability of PV-electrochemical integration, the study aims to provide insights that could accelerate the adoption of hydrogen as a clean energy carrier.

In summary, the activity was driven by the need to find efficient, sustainable, and cost-effective methods for hydrogen production, leveraging the potential of PV technology in the process.

Expected results and deliverables

- 1. Efficient solar-to-hydrogen conversion:** The case study is expected to demonstrate advancements in PV electrochemical integration for water-splitting, focusing on achieving higher STH conversion efficiency. This would contribute to the development of sustainable and cost-effective methods for hydrogen production.
- 2. Optimization of materials and processes:** By analyzing various materials and processes used in PV and electrochemical cells, the study aims to identify the most efficient combinations. This optimization can lead to improved performance and stability, benefiting future research and industrial applications.
- 3. Scalability and practical implementation:** The study will explore the scalability of the integrated system, assessing its potential for large-scale implementation. Insights gained from this can guide the design of commercial hydrogen production systems.
- 4. Environmental impact assessment:** The case study will provide an analysis of the environmental benefits of using renewable energy sources for hydrogen production. This includes reducing carbon emissions and minimizing the ecological footprint of the energy production process.
- 5. Cost-benefit analysis:** A detailed cost-benefit analysis will be conducted to evaluate the economic viability of the integrated system. This will help stakeholders understand the financial implications and potential returns on investment in PV electrochemical water-splitting technologies.

Reader benefits

- 1. Comprehensive understanding:** Readers will gain a comprehensive understanding of the latest advancements in PV electrochemical integration for water-splitting, including the underlying principles, materials, and processes involved.
- 2. Practical insights:** The case study will provide practical insights into the optimization and implementation of such systems, offering guidance for researchers, engineers, and industry professionals.

3. **Informed decision-making:** By presenting a detailed cost-benefit analysis and environmental impact assessment, the case study will enable readers to make informed decisions about investing in or adopting these technologies for sustainable energy production.
4. **Future research directions:** The study will highlight areas where further research is needed, helping to shape the direction of future studies and innovations in the field of renewable energy and hydrogen production.

18.7.5 Safety considerations

When integrating PV and electrochemical systems for water-splitting, safety considerations are crucial to the project's success. Here are key safety aspects that the reader must be aware of:

1. Electrical safety

- **High voltage risks:** The combination of PV panels and electrochemical cells can generate high voltages, especially under optimal sunlight conditions. Proper insulation, grounding, and circuit protection (like fuses and circuit breakers) are essential to prevent electric shock or short circuits.
- **Overcurrent protection:** Given the variability of solar energy, the system must include overcurrent protection to safeguard against potential surges that could damage equipment or cause fires.

2. Chemical safety

- **Handling of electrolytes:** Electrolytes used in water-splitting systems can be corrosive or toxic. Proper storage, handling, and disposal of these chemicals are essential. Personal protective equipment (PPE) such as gloves, goggles, and lab coats should be used when dealing with electrolytes.
- **Gas management:** The process generates hydrogen and oxygen gases, which can be explosive if mixed in the wrong proportions. Ensuring proper ventilation and gas separation is critical. The design should include pressure relief valves and fail-safes to avoid gas buildup.

3. Thermal safety

- **Heat generation:** Both PV panels and electrochemical cells can produce significant amounts of heat during operation. This necessitates adequate cooling systems to prevent overheating, which could lead to thermal runaway or equipment failure.
- **Fire prevention:** The combination of electrical and chemical components poses a fire risk. Fire suppression systems should be in place, and all materials used should be flame-retardant.

4. Structural integrity

- **Material compatibility:** Ensure that materials used in the construction of the PV and electrochemical systems are compatible and resistant to corrosion, especially in humid or outdoor environments.
- **Load bearing:** The structure supporting the PV panels and electrochemical cells should be capable of handling the weight and any dynamic forces, such as wind or seismic activity.

5. Environmental and health safety

- **Waste management:** Proper protocols must be in place for the disposal of chemical waste and decommissioned components, considering the environmental impact.
- **Exposure to sunlight:** Prolonged exposure to sunlight during installation or maintenance can pose risks such as heatstroke or UV damage to workers. Adequate shade, hydration, and sunscreen should be provided.

6. Regulatory compliance

- **Adherence to standards:** The system must comply with local, national, and international safety standards, including electrical codes, chemical handling regulations, and environmental laws.
- **Permitting and inspections:** Before starting the project, ensure that all necessary permits are obtained, and regular inspections are scheduled to maintain safety standards throughout the project's lifecycle.

These safety considerations are critical to minimizing risks and ensuring the safe and successful implementation of a PV electrochemical water-splitting system.

18.7.6 Actions taken/Workflow/Tools used/Simulations and analyses

Photovoltaic electrochemical integration for water-splitting is an advanced method combining PV cells with electrochemical systems to convert sunlight into chemical energy, primarily in the form of hydrogen through water-splitting. This case study explores the actions taken, workflow, tools used, simulations, and analyses performed in a research setting aimed at optimizing this technology.

1. Understanding the problem statement

Objective:

The primary goal is to integrate PV cells with an electrochemical system for efficient water-splitting to generate hydrogen. The study focuses on optimizing the efficiency of the system and analyzing the performance under different conditions.

2. Literature review and initial planning

Actions taken:

- Reviewed existing literature on PV-EC systems, focusing on the types of PV cells (e.g., silicon-based, perovskite) and electrochemical catalysts used for water-splitting.
- Identified key parameters influencing system efficiency, including light absorption, charge carrier dynamics, and catalyst efficiency.

Tools used:

- **Zotero** for managing research papers and references.
- **Mendeley** for collaborative reference management.

3. System design and selection of materials

Step 1: Selection of photovoltaic cells

- Evaluated different PV materials for their efficiency, cost, and compatibility with electrochemical systems.

- Selected a high-efficiency perovskite solar cell based on its superior light absorption and ease of integration with electrochemical cells.

Step 2: Selection of electrochemical catalysts

- Explored various catalysts like platinum (Pt), iridium oxide (IrO₂), and nickel-iron (NiFe) for the OER and HER.
- Chose NiFe as the catalyst due to its cost-effectiveness and relatively high efficiency.

Tools used:

- **Material Studio** for computational material selection and initial simulations.
- **COMSOL Multiphysics** for modeling the integration and simulation of electrochemical processes.

4. Simulation and modeling

Step 3: Photovoltaic cell simulation

- Simulated the PV cell's performance under standard sunlight conditions to determine the voltage and current characteristics.

Step 4: Electrochemical cell simulation

- Modeled the electrochemical reactions within the cell to optimize the electrode design and catalyst placement.

Step 5: Integrated system simulation

- Combined the PV and EC models to simulate the integrated system's performance.
- Analyzed the effect of varying light intensity, temperature, and electrolyte concentration on system efficiency.

Tools used:

- **MATLAB®/Simulink** for system-level simulation and optimization.
- **Ansys** for finite element analysis to understand the thermal and stress behavior within the system.

Workflow:

1. **Initial setup:** Define the problem and gather necessary materials.
2. **Material selection:** Choose the appropriate PV material and electrochemical catalysts.
3. **Simulation:** Perform individual simulations of PV and EC systems.
4. **Integration:** Combine PV and EC systems into a single model.
5. **Optimization:** Refine system parameters to maximize efficiency.
6. **Validation:** Compare simulated results with experimental data.

5. Experimental validation

Step 6: Prototype development

- Constructed a small-scale prototype based on the optimized simulation model.
- Tested the prototype under controlled lab conditions to measure hydrogen production efficiency.

Step 7: Data collection and analysis

- Collected data on voltage, current, hydrogen production rate, and system stability.
- Compared the experimental results with the simulated predictions to validate the model.

Tools used:

- **LabVIEW** for data acquisition and real-time monitoring.
- **OriginPro** for data analysis and graphing.

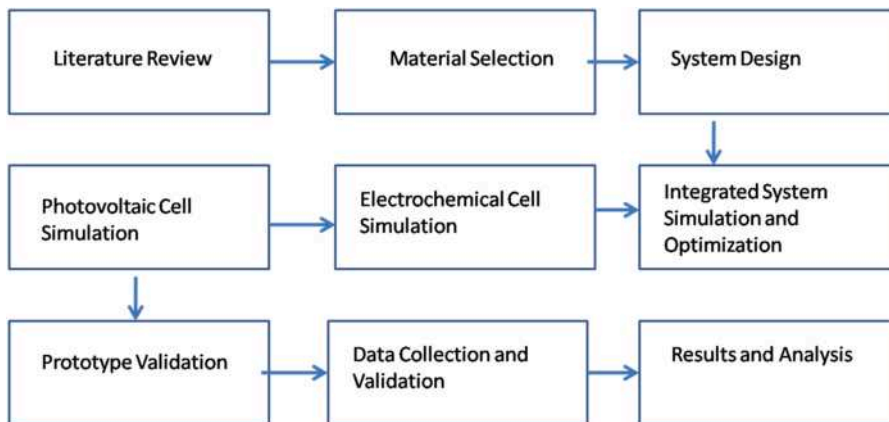
6. Results and discussion

- **Efficiency analysis:** Discussed the overall efficiency of the integrated PV-EC system, highlighting the key factors that contributed to the observed performance.
- **Challenges and solutions:** Identified challenges such as system stability, degradation of materials, and energy losses, along with proposed solutions.
- **Future Work:** Suggested areas for further research, including exploring new materials and optimizing system design.

7. Conclusion

The study successfully demonstrated the integration of PV cells with electrochemical systems for water-splitting, achieving a significant improvement in hydrogen production efficiency. The use of advanced simulation tools and careful material selection were key to the project's success.

Flowchart



This detailed case study should provide a comprehensive understanding of the steps taken in the PV-EC integration process for water-splitting.

18.7.7 Challenges and solutions

Photovoltaic electrochemical water-splitting is a promising technology for sustainable hydrogen production. The process involves using sunlight to drive the electrolysis of water, producing hydrogen and oxygen. However, the integration of PV and electrochemical systems for efficient and cost-effective water-splitting faces several challenges. Below are some of the key challenges and potential solutions that have been explored in case studies and research:

18.7.8 Challenges

1. Efficiency mismatch:

- **Challenge:** The efficiency of PV cells and the electrochemical processes often do not match. PV cells might produce more electricity than the electrochemical cell can use efficiently, leading to losses.
 - **Solution:** Researchers are exploring tandem solar cells, which combine different materials to absorb a broader range of the solar spectrum, increasing overall efficiency. Power management strategies that involve buffering and matching the power output of the PV cells to the needs of the electrochemical process are also being developed.
- 2. Stability and durability:**
- **Challenge:** The materials used in both the PV and electrochemical systems can degrade over time, especially under harsh operating conditions such as high temperatures or corrosive environments. This degradation reduces the system's lifespan and efficiency.
 - **Solution:** The development of more robust materials, such as corrosion-resistant catalysts and encapsulation techniques to protect PV cells, is crucial. Advances in material science are also focusing on improving the stability of photoelectrodes used in the process.
- 3. Cost:**
- **Challenge:** The high cost of materials, such as catalysts for the electrochemical reactions and high-efficiency PV cells, makes the overall system expensive.
 - **Solution:** Cost reduction can be achieved through the use of earth-abundant materials, improving manufacturing processes, and scaling up production. Researchers are also looking into cheaper, more efficient catalysts, such as those based on transition metal oxides instead of Pt.
- 4. Integration complexity:**
- **Challenge:** Integrating PV and electrochemical systems requires complex engineering to ensure that the two components work together efficiently. This includes challenges in power management, heat management, and system optimization.
 - **Solution:** Integrated system designs that optimize the interaction between PV and EC components are being developed. Computational models and simulations are also used to predict and improve system performance before physical prototypes are built.
- 5. Intermittency of solar energy:**
- **Challenge:** The intermittent nature of solar energy (e.g., night-time or cloudy days) makes it difficult to achieve consistent hydrogen production.
 - **Solution:** Hybrid systems that integrate energy storage solutions, such as batteries or other forms of energy storage, can smooth out the supply and ensure continuous operation. Additionally, the development of more efficient energy storage methods for hydrogen itself is an ongoing area of research.

18.7.9 Solutions uncovered

While these challenges are significant, ongoing research has led to several promising solutions:

- **Use of tandem cells:** Tandem cells that combine perovskite with silicon have shown higher efficiency in converting sunlight to electricity, which can then be used for water-splitting.
- **Advanced catalysts:** The development of nonprecious metal catalysts, such as NiFe alloys, has reduced costs while maintaining high catalytic activity for water-splitting.
- **System integration:** Improved design of integrated PV-EC systems, with better thermal management and more efficient power electronics, has enhanced overall system performance.
- **Energy storage:** The integration of energy storage solutions like batteries or hydrogen storage tanks helps in dealing with the intermittency of solar power.

These solutions are still in development, and large-scale implementation will require further advancements in technology, cost reductions, and more extensive field testing. However, the progress so far has been promising, with several pilot projects demonstrating the feasibility of PV-EC water-splitting as a sustainable hydrogen production method.

18.7.10 Results

Photovoltaic electrochemical integration for water-splitting is a cutting-edge approach that combines PV cells with electrochemical systems to directly convert sunlight into chemical energy, particularly for splitting water into hydrogen and oxygen. The results of case studies on this technology typically focus on efficiency, stability, and scalability.

18.7.11 Outcomes of PV-EC integration for water-splitting

1. Efficiency:

- **Expected:** The primary goal of PV-EC systems is to achieve high STH efficiency. Theoretically, STH efficiencies of 15–20% or higher are considered highly desirable.
- **Actual:** Many case studies report STH efficiencies ranging from 10% to 19%, depending on the specific materials and design used. This is generally within expected ranges, though ongoing research aims to push these efficiencies higher.

2. Stability and durability:

- **Expected:** Long-term stability under operational conditions is crucial for practical applications. A stable system would operate effectively over months or years without significant degradation.
- **Actual:** Case studies often report stability challenges, particularly in the harsh conditions required for water-splitting. Some systems maintain stability for thousands of hours, while others experience rapid degradation, which can be a limiting factor.

3. Scalability:

- **Expected:** The ability to scale up the technology for industrial use is a significant consideration. Laboratory-scale efficiencies may not always translate directly to larger systems.
- **Actual:** Case studies show that while small-scale systems demonstrate promising results, scaling up can introduce new challenges, such as increased costs and reduced

efficiency. However, some studies report successful scale-up with minimal losses in performance.

4. Cost:

- **Expected:** Reducing the cost of materials and manufacturing processes is critical to making PV-EC systems commercially viable.
- **Actual:** While some case studies indicate that costs are still high, ongoing research and development are focused on using cheaper materials and more efficient manufacturing techniques. Some success has been reported in reducing costs, though significant challenges remain.

18.7.12 Were the outcomes expected?

- **Partially:** Many outcomes align with theoretical predictions, particularly in terms of efficiency and initial performance. However, challenges related to long-term stability, scalability, and cost have been more difficult to overcome than expected. Researchers are continuing to refine materials and system designs to address these issues.

In summary, while the outcomes of PV-EC integration for water-splitting are promising, they also highlight the need for continued research to address the challenges that remain before this technology can be widely adopted.

18.7.13 Learning and knowledge outcomes

1. Learning and knowledge outcomes:

- **Integration benefits:** The case study likely highlighted the synergy between PV cells and electrochemical water-splitting. Combining PV systems with electrochemical cells can enhance the efficiency of converting solar energy into hydrogen, a clean fuel.
- **System efficiency:** Insights into how the efficiency of PV electrochemical systems can be optimized, including the impact of different materials, system designs, and operational conditions on hydrogen production rates.
- **Material compatibility:** Understanding the importance of selecting appropriate materials for both the PV cells and the electrochemical cell components to ensure long-term stability and performance.
- **Economic and environmental impact:** The potential for reducing costs and environmental impacts compared to traditional energy sources, as well as the scalability of these systems for practical applications.

2. What could have been done differently:

- **Experimental design:** More rigorous experimental setups and controls might have been used to isolate variables and accurately measure system performance under varying conditions.
- **Long-term testing:** Extended testing over longer periods could provide a better understanding of the durability and stability of the integrated system.
- **Broader material testing:** Exploring a wider range of materials for both the PV cells and the electrochemical components might reveal more efficient or cost-effective alternatives.

3. What mustn't be changed:

- **Focus on integration:** The emphasis on integrating PV systems with electrochemical cells should remain, as it is central to the innovation and potential of this approach.
- **Sustainability goals:** The focus on sustainability and clean energy solutions is crucial and should continue to drive future research and development efforts.

4. Recommendations for future investigation:

- **Advanced materials research:** Investigate new and improved materials that could enhance efficiency, reduce costs, or improve the longevity of the integrated systems.
- **System optimization:** Focus on optimizing system designs for different scales, from small-scale applications to larger, industrial-scale systems.
- **Economic analysis:** Conduct comprehensive economic analyses to better understand the cost-effectiveness and market viability of PV electrochemical integration.
- **Integration with other technologies:** Explore how this integration can be combined with other renewable energy technologies or energy storage systems to create more comprehensive and resilient energy solutions.

These aspects will help in refining the current understanding of PV electrochemical integration for water-splitting and drive advancements in the field.

18.8 Conclusion

The integration of photovoltaic technology with electrochemical water splitting offers a sustainable and efficient approach to hydrogen production. By harnessing solar energy, this method decreases dependence on fossil fuels and reduces greenhouse gas emissions, making a substantial contribution to renewable energy efforts. Advances in PV materials and electrochemical catalysts have significantly improved the overall efficiency of the water-splitting process. High-efficiency PV cells combined with effective electrocatalysts ensure better solar-to-hydrogen conversion rates, making the technology more viable for large-scale applications. The use of renewable solar energy for hydrogen production significantly reduces the environmental footprint compared to conventional methods. By minimizing carbon emissions and reducing dependence on non-renewable resources, PV-assisted water splitting bolsters worldwide initiatives to address climate change and advance sustainable development. Ongoing research is focused on further improving the efficiency and durability of both PV cells and electrochemical catalysts. Innovations in materials science, such as the development of new semiconductor materials and novel catalyst designs, are expected to drive further advancements. Additionally, integrating PV-assisted water splitting with other renewable energy systems, like wind and biomass, could enhance overall energy efficiency and storage capabilities. Although considerable advancements have been achieved, challenges persist regarding energy conversion efficiency, system stability, and economic competitiveness. Addressing these challenges requires continued interdisciplinary research and collaboration among scientists, engineers, and policymakers. Incentives for renewable energy adoption and supportive regulatory frameworks will also play crucial roles in overcoming these barriers.

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Photochemical Splitting of Water

Fundamentals to Applications

Photochemical Splitting of Water: Fundamentals to Applications brings together the very latest information on photochemical water splitting for hydrogen production, covering basic concepts, mechanisms, instrumentation, experimental set-up, analysis, materials used as catalysts, innovative methods, and future opportunities.

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