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MEng Thesis

**HYDROGEN ENERGY: ADVANCES IN NANOTECHNOLOGY FOR HYDROGEN
STORAGE**

by

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ΤΗΝ ΑΠΟΘΗΚΕΥΣΗ ΥΔΡΟΓΟΝΟΥ**

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Abstract

Hydrogen has been unequivocally recognized as a significant carrier of energy due to its excellent attributes over traditional and other sources of energy. Foremost characteristics include its low mass density, ease in handling, large energy value per unit of mass (approximately 142 MJ/kg), and cost-effectiveness with minimal contribution to the environment. Hydrogen's unique fuel attributes render it as a potential replacement for traditional fossil fuels. The use of hydrogen in energy production and other energy applications, including the transport sector, is greatly preferred due to its nature as a clean energy carrier. Nevertheless, the lack of proper storage technologies has been the primary limitation to the wider application of hydrogen in these industries. Hydrogen is very versatile as a fuel and can be produced from numerous feedstocks, including biodiesel, gasoline, and methane, among others.

Hydrogen can generate energy with minimal greenhouse gas emissions if produced sustainably, which makes it an attractive option as a renewable energy carrier. The shift from traditional fossil fuels to green hydrogen represents a significant transformation in energy paradigms, carrying extensive consequences for global energy markets.

The rapidly changing geopolitical environment, coupled with continuous technological advancements, underscores the significance of sustainable energy security. Research suggests that electrochemical energy systems hold considerable promise in addressing various challenges related to energy conversion, storage, and conservation, while achieving high efficiency and minimal pollution. This study offers a comprehensive overview of electrochemical energy devices and the diverse optimization techniques employed in their evaluation. To cater to the increasing interest in this field, most of the study concentrates on a review of the most promising and extensively researched electrochemical energy devices, including fuel cells, batteries, and supercapacitors. Additionally, the paper provides a brief discussion on hydrogen production technologies, electrochemical reactors, and membrane separation technologies, among others. As the global community confronts the challenges of climate change and the quest for sustainable energy solutions, it is essential for executives, policymakers, and stakeholders to consider these critical issues.

Περίληψη

Το υδρογόνο έχει αναμφισβήτητα αναγνωριστεί ως σημαντικός φορέας ενέργειας λόγω των εξαιρετικών ιδιοτήτων του έναντι των παραδοσιακών και άλλων πηγών ενέργειας. Τα κυριότερα χαρακτηριστικά περιλαμβάνουν τη χαμηλή πυκνότητα μάζας, την ευκολία χειρισμού, τη μεγάλη ενεργειακή αξία ανά μονάδα μάζας (περίπου 142 MJ/kg) και τη σχέση κόστους-αποτελεσματικότητας με ελάχιστη συμβολή στο περιβάλλον. Τα μοναδικά χαρακτηριστικά καυσίμου του υδρογόνου το καθιστούν πιθανό υποκατάστατο των παραδοσιακών ορυκτών καυσίμων. Η χρήση του υδρογόνου στην παραγωγή ενέργειας και σε άλλες ενεργειακές εφαρμογές, συμπεριλαμβανομένου του τομέα των μεταφορών, προτιμάται σε μεγάλο βαθμό λόγω της φύσης του ως φορέα καθαρής ενέργειας. Ωστόσο, η έλλειψη κατάλληλων τεχνολογιών αποθήκευσης ήταν ο πρωταρχικός περιορισμός στην ευρύτερη εφαρμογή του υδρογόνου σε αυτές τις βιομηχανίες. Το υδρογόνο είναι πολύ ευέλικτο ως καύσιμο και μπορεί να παραχθεί από πολλές πρώτες ύλες, όπως το βιοντίζελ, η βενζίνη και το μεθάνιο, μεταξύ άλλων.

Το υδρογόνο μπορεί να παράγει ενέργεια με ελάχιστες εκπομπές αερίων του θερμοκηπίου εάν παράγεται με βιώσιμο τρόπο, γεγονός που το καθιστά ελκυστική επιλογή ως φορέα ανανεώσιμης ενέργειας. Η στροφή από τα παραδοσιακά ορυκτά καύσιμα στο πράσινο υδρογόνο αντιπροσωπεύει έναν σημαντικό μετασχηματισμό των ενεργειακών παραδειγμάτων, με εκτεταμένες συνέπειες για τις παγκόσμιες αγορές ενέργειας.

Το ταχέως μεταβαλλόμενο γεωπολιτικό περιβάλλον, σε συνδυασμό με τις συνεχείς τεχνολογικές εξελίξεις, υπογραμμίζει τη σημασία της βιώσιμης ενεργειακής ασφάλειας. Η έρευνα δείχνει ότι τα ηλεκτροχημικά ενεργειακά συστήματα υπόσχονται πολλά για την αντιμετώπιση διαφόρων προκλήσεων που σχετίζονται με τη μετατροπή, την αποθήκευση και τη διατήρηση της ενέργειας, επιτυγχάνοντας παράλληλα υψηλή απόδοση και ελάχιστη ρύπανση. Αυτή η μελέτη προσφέρει μια ολοκληρωμένη επισκόπηση των ηλεκτροχημικών ενεργειακών συσκευών και των διαφορετικών τεχνικών βελτιστοποίησης που χρησιμοποιούνται για την αξιολόγησή τους. Για να καλυφθεί το αυξανόμενο ενδιαφέρον σε αυτόν τον τομέα, η πλειοψηφία της μελέτης επικεντρώνεται σε μια ανασκόπηση των πιο πολλά υποσχόμενων και εκτενώς ερευνημένων ηλεκτροχημικών ενεργειακών συσκευών, συμπεριλαμβανομένων κυψελών καυσίμου, μπαταριών και υπερπυκνωτών. Επιπλέον, στην παρούσα εργασία γίνεται συζήτηση για τις τεχνολογίες παραγωγής υδρογόνου, τους ηλεκτροχημικούς αντιδραστήρες και τις τεχνολογίες διαχωρισμού μεμβράνης, μεταξύ άλλων.

Καθώς η παγκόσμια κοινότητα αντιμετωπίζει τις προκλήσεις της κλιματικής αλλαγής και την αναζήτηση βιώσιμων ενεργειακών λύσεων, είναι σημαντικό τα στελέχη, οι υπεύθυνοι χάραξης πολιτικής και οι ενδιαφερόμενοι φορείς να εξετάσουν αυτά τα κρίσιμα ζητήματα.

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CHAPTER 1

Introduction

Nowadays, the generation and conversion of energy stand as one of the essential requirements within human society. Fossil fuels serve as a major energy source; however, their combustion presents a considerable challenge due to the triggering of climate change. These fuels contribute to environmental degradation and are classified as non-renewable resources. The swift rise in population has intensified the necessity for sustainable energy solutions. Consequently, developing countries must urgently seek practical, cost-effective, clean, and renewable alternatives to fossil fuels.

Theoretically, hydrogen and electricity can fulfill the energy needs of the world, facilitating the development of an energy system that is self-sufficient and does not rely on traditional energy sources. Hydrogen is rarely found in its pure form; it functions as an energy carrier that can store, and release energy sourced from fossil fuels and renewable energy sources (RES). This energy can subsequently be converted into electricity and heat through fuel cells or combustion engines.

The combustion of hydrogen or its interaction with oxygen yields only water vapor as a byproduct, establishing it as a clean alternative to fossil fuels. This characteristic is particularly significant in efforts to reduce air pollution, as it results in the complete absence of greenhouse gas emissions. Furthermore, green hydrogen, generated from renewable sources such as water electrolysis and biomass conversion, is increasingly recognized as a vital component of decarbonization initiatives. As a result, the adoption of hydrogen and hydrogen-derived fuels is emerging as a promising strategy for achieving net-zero emissions.

This study outlines both standard and advanced hydrogen storage technologies, including physical storage, material-based adsorption, and material-based absorption. Physical storage methods, such as compressed gas hydrogen, liquid hydrogen, and cryo-compressed hydrogen, have proven to be technically viable solutions for large-scale applications across multiple sectors. However, various challenges associated with physical storage technologies, including safety issues, high costs of storage vessels, and energy-intensive processes, limit their broader adoption and advancement. In recent decades, material-based adsorption and absorption techniques have garnered significant attention for hydrogen storage, primarily due to their advantages, such as strong stability and high volumetric density. Material-based absorption (chemisorption) involves the chemical bonding of hydrogen atoms through reactions with metal hydrides or chemical hydrides, yielding high storage capacity and stable properties. Nevertheless, several challenges, including high dehydrogenation temperatures, slow reaction kinetics, environmental concerns, and unresolved cost factors, remain to be addressed.

In chapter 2, catalysis and electrocatalysis will be described along with electrochemical

devices primarily designed for hydrogen storage.

In chapter 3, the electrolysis of water and hydrogen economy will be discussed.

In chapter 4, advancements in nanomaterials for hydrogen storage will be analyzed.

Finally, in chapter 5, conclusions and perspectives on the future development of materials for hydrogen storage will be presented.

CHAPTER 2

Catalysis, Electrocatalysis & Electrochemical devices for hydrogen conversion and storage

2.1 Introduction

Urbanization and the expansion of human population have markedly increased global energy demands, leading to environmental challenges such as ecosystem degradation, acid rain, air pollution, global warming, and the depletion of energy resources. This reality underscores the urgent need to explore alternative energy sources derived from renewable resources. The integration of renewable energy sources (RES)—such as solar, wind, biomass, and geothermal—with artificial intelligence (AI) methodologies has resulted in significant advancements in hydrogen production. These innovations not only address the variability of renewable energy outputs but also facilitate the efficient and sustainable generation of hydrogen, meeting the growing demand for clean fuel options.

The risks and realities of environmental deterioration have become increasingly evident, due to various interrelated factors. The dramatic growth of the global population, energy consumption, industrial activity, and associated human activities has amplified the environmental consequences. During the 1970s most environmental analysis and legal control measures focused on conventional pollutants such as sulfur dioxide (SO_2), nitrogen oxides (NO_x), particulates, and carbon monoxide (CO). More recently, environmental concerns have expanded to include the regulation of micro - or hazardous air pollutants-often toxic chemical substances and harmful in small doses-as well as globally significant pollutants like carbon dioxide (CO_2). In addition to advances in environmental science, developments in industrial processes and infrastructures have introduced new environmental challenges. For example, in the energy sector, the shift toward road transport of industrial goods and individual car travel has increased road traffic and redirected attention to the effects and sources of NO_x and volatile organic compound (VOC) emissions [1].

Given these challenges, energy is recognized as a critical factor that must be addressed through various measures, including the need for a sustainable and secure supply of energy resources. Achieving a secure energy supply is widely acknowledged as essential [1].

A continuous increase in the contribution of intermittent RES to power generation is evident worldwide. Simply connecting RES to the power grid does not always indicate that all the generated electricity will reach end consumers. The power grid, which connects energy generation with demand, is a complex system governed by physical laws. A common characteristic of many power systems is the replacement of conventional technologies with RES, necessitating significant changes in electricity flow patterns across the grid [2].

The rising demand for advanced energy solutions to satisfy global energy requirements is

driving advancements in energy storage, conversion, and generation technologies. Economic considerations related to power generation and distribution across extensive energy grids highlight the importance of developing superior energy storage systems for load leveling and peak load management.

Current research in the electrochemical field focuses on the study and optimization of electrode and electrolyte materials, electrochemical properties and their integration into functional assemblies. Electrochemical devices play a critical role in emerging markets, with system performance relying on the properties of electrodes and electrolytes. While primary electrochemical properties are optimized for specific applications, secondary properties, including chemical stability and mechanical characteristics such as strength, toughness, thermal expansion, cost-effectiveness, and temperature tolerance, are equally important. State-of-the-art electrochemical devices include high-energy-density batteries, fuel cells, membrane reactors, and gas separation devices. Contemporary technological challenges include a diminishing supply of lithium, essential for widely used lithium-ion batteries (LiBs). Fuel cells face issues of low reliability and durability. Hydrogen production is constrained by high costs and strict storage requirements. Moreover, challenges such as low production rates and stability issues in membrane electrode assemblies for CO₂ conversion persist, alongside broader difficulties related to scaling up technologies and bridging the gap between end-user needs and existing solutions [3].

2.2 Catalysis / Electrocatalysis

The Swedish chemist Berzelius was the first to employ the term "catalysis" in 1835. The term was used more appropriately some years later by Ostwald, who explained in 1894: "Catalysis is the acceleration of a slow chemical process by the presence of a foreign material." The theory is currently defined as the process by which a slow chemical reaction is accelerated through the addition of an outside substance, a catalyst. A catalyst speeds up the reaction by reducing the activation energy of the reaction, typically by its interaction with the reactant molecules [4].

Over a century later, it is widely accepted that a catalyst speeds up the rate of reaction by reducing the activation energy required for the process. This occurs since the catalyst briefly interacts with the molecules of the reactants in a way that interaction increases the rate of reaction. Though a participant in the reaction process, the catalyst does not experience any change, hence can mediate the change of numerous molecules. So, only a small catalytic quantity of the substance is needed to initiate large-scale chemical change. Despite its pivotal position in contemporary chemistry, introductory textbooks usually give an inadequate description of the refined mechanisms involved in catalysis, presenting merely a simplistic overview of its principles. Nevertheless, catalysis is at the core of contemporary chemistry since one or more steps involving catalysis are included in the synthesis of practically all chemical substances. Over the past century, catalysis has profoundly influenced both industrial applications and academic research. However, for much of

its history, catalysis was regarded more as an art than as a rigorous scientific discipline [4].

2.2.1 Electrocatalysis / Historical aspects

Electrocatalysis is a specialized area within electrochemical kinetics, with its origins remaining a topic of discussion regarding the initial contributors, as noted in Trasatti's commentary on water electrolysis[5]. The development of electrocatalysis can be traced to quantitative evaluations of electrocatalytic reaction rates, exemplified by the 1928 publication of Bowden and Rideal[6]. In their work they characterized activity in terms of current density at a specific electrode potential. Frumkin expanded this concept by defining activity as the reaction rate constant measured at a consistent potential relative to a reference electrode, accounting for electrostatic "double layer" effects. Both studies primarily address hydrogen evolution, which has historically been regarded as the quintessential model for electrocatalytic processes. They demonstrated the profound influence of electrode material composition on electrocatalytic activity, a topic extensively reviewed by Appleby[7].

An alternative perspective on the history of electrocatalysis suggests that it commenced with the initial observations of processes later recognized as electrocatalytic. Electrocatalysis term could be said to begin with Nicholson and Carlisle's work in 1800, or even to Volta's earlier concept of water electrolysis. Moreover, Davy's work in 1802 concerning electricity generation from chemical reactions are now viewed as precursors to fuel cell electrocatalysis. Earlier experiments conducted by Paets van Troostwijk in 1789 [5], are not typically classified as electrocatalysis due to the extremely high voltage produced by the triboelectric generator. This raised discharges between closely spaced electrodes and resulted in water decomposition rather than true electrocatalytic water splitting [8], [9].

The origins of electrocatalysis can reasonably be traced back to the late 19th century, a period marked by both observational and quantitative research on reaction rates. In 1898, Haber's publication compiled experimental data on a diverse array of electrode reactions, now classified as electrocatalytic. Large-scale industrial processes, such as the production of chlorine and hypochlorite, alongside smaller-scale processes like the electrosynthesis of various inorganic and organic compounds were included. Additionally, original studies by Tafel (1900) and Haber (1904) [7] examined catalytic efficiency, measured as the overpotential at a specific current density, which can be interpreted as a contemporary measure of electrocatalytic activity. The term 'efficiency' was established in the early 20th century, as illustrated by Foerster's 1905 treatise on the electrochemistry of aqueous solutions [9].

The term "electrocatalysis" emerged later and is essentially a combination of "electro" and "catalysis." As noted by Frumkin et al., it appears that Kobosew and Monblanowa [10] were the first to introduce this term, with references to their work in 1930s. Kobosew's initial contribution

in 1930 involved establishing a relationship between hydrogen-metal bond energy and overpotential. While earlier uses of the term "electrocatalysis" have been identified, they do not explicitly pertain to "the determination of reaction rates at a given potential," which is the main subject in recent research [8].

The historical groundwork of electrocatalysis, as presented in the literature by Haber and Foerster[7], serve as the cornerstone for various electrocatalytic processes that remain pertinent nowadays. The need of practical applications frequently stimulates the development of new knowledge concerning particular reactions or systems. However, the essential pathways of electrocatalysis have remained relatively constant, and their complexity continues to obstruct the characterization of electrocatalysis as a quantitatively predictable phenomenon. Electrocatalytic reactions are inherently multistep processes, requiring significant effort to ascertain which elementary step is the rate-limiting factor. This complexity is further compounded when multiple parallel reaction pathways exist, with their adsorbed intermediates competing for limited adsorption sites. In the case of critical electrocatalytic reactions, such as the oxygen reduction reaction (ORR), organic fuel oxidation, and reductive hydrogenation, the full sequence of elementary steps is difficult to articulate. To mitigate this complexity, formal kinetics is typically used, relying on simplified reaction schemes that do not claim to accurately depict elementary events and their associated transition states. In this framework, each step is characterized by a formal rate constant, which is assumed to be independent of the potential [7].

The electrode potential is crucial in determining the free charge of the electrode, which impacts the state and reactivity of adsorbates. Unfortunately, the relationship between potential and free charge is largely unexplored for most "new catalysts," adding complexity to understanding the term of electrocatalysis. However, focusing on model systems, whether regarding reactions, catalysts, or both, that are simpler can offer better fundamental insights, even if they may not be directly applicable in practical scenarios [11].

The range of model catalysts is limited to a few metals and oxides; however, the variety of electrocatalysts being studied has expanded considerably over the last four decades. This evolution in materials has occurred in two primary dimensions: structurally, as the focus has shifted from model single crystals and specifically selected nanoparticles to a broader array of nanoporous materials and composites; and chemically, as the scope has shifted from single-phase metals and binary compounds to encompass multi-element alloys and a diverse array of compounds across the periodic table. Additionally, the integration of these materials into electrode highlights the use of binders and conductive additives, thereby complicating the overall system [12]. This complexity is further amplified by an approach that emphasizes practical considerations, such as reducing the cost of electrocatalytic materials, repurposing existing materials for different reactions, or exploring innovative methods through empirical

experimentation. This aspect must be balanced with a commitment to traditional scientific principles to mitigate potential errors. The latter approach begins with a thorough investigation of the fundamental characteristics of electrocatalytic reactions and the atomic or molecular structure of the interfacial region where these reactions occur [13].

2.2.2 From heterogenous catalysis to electrocatalysis

The following section focuses on the processes occurring at the electrode-electrolyte interface. These processes exhibit clear similarities with heterogeneous catalysis, particularly due to the presence of adsorbed reaction intermediates. Other areas of electrocatalysis involve fundamentally distinct processes, such as mediator electrocatalysis, which includes homogeneous chemical reactions in solution, as well as electrocatalysis occurring at liquid/liquid and electrode/solid electrolyte interfaces, the latter primarily focusing on high-temperature processes, and photo electrocatalysis [7].

Heterogeneous catalysis occurs at the surface of a solid. Therefore, the materials with a large surface area, i.e. fine powders or porous solids, make better use of the catalytic material and are more efficient than large single crystals. However, for porous materials there is frequently a subject of discussion, whether catalytic activity is restricted to the outer surface or whether the surface inside the pores contributes. Furthermore, the preference for nanometer over micrometer size catalytic particles is not only a question of the economy, making better use of expensive materials like platinum metal. Small particles have a larger fraction of their atoms on the surface, and moreover, an atom on the surface of a small metal particle has electronic properties which are significantly different from those on the surface of a large particle [14].

Heterogeneous catalysis, intricately connected to surface science—a domain within condensed matter physics—has significantly influenced the advancement of electrocatalysis [15]. Over time, both disciplines have developed in a manner that fosters reciprocal influence. This interaction can be summarized as follows:

- These two fields interact through phenomenological kinetic models that originate from the Langmuir period, while retaining their individual differences. These differences are attributed to the diverse approaches to catalysis control: temperature governs heterogeneous catalysis, while electrode potential governs electrocatalysis. Consequently, heterogeneous catalysis is primarily linked to surface science, in contrast to electrocatalysis, which is primarily linked to interfacial electrochemistry [16].
- Both fields are interconnected with chemical physics; however, the utilization of microscopic theory related to electron transfer reactions is constrained by the intricate nature of the reaction zone and the multistep pathways involved in electrocatalysis. Existing theoretical frameworks are primarily focusing on electron transfer, proton transfer, and the coupled transfer of protons and

electrons. The application of quantitative theory to actual electrocatalytic reactions generally needs computational efforts to derive the required parameters [17].

- Substantial advancements have been made in the computational modeling of intermediates and certain fundamental steps on 'wet' surfaces, particularly in the context of free energy diagrams along the reaction coordinate. This approach can address both single crystalline surfaces and more complex surfaces with varying local coordination. However, it often neglects to account for solvation, 'double layer' effects, and the kinetics associated with reactions. Electrocatalysis requires more intensive efforts compared to computational heterogeneous catalysis, as adlayers are typically multicomponent and interfaces are charged. Consequently, further development is necessary to enhance the predictability of this field and to reduce misinterpretations arising from a limited understanding of the current models' limitations. Recent initiatives aimed at incorporating electrostatic effects appear promising [14].
- In order to systematically tackle the discrepancies of observed phenomena, both heterogeneous catalysis and electrocatalysis employ precisely defined model catalysts.
- Progress in in situ spectroscopic, diffraction, and microscopic methodologies have propelled and will persist in impelling novel discoveries in both heterogeneous catalysis and electrocatalysis. This progress takes place despite the more complex technical difficulties linked to catalyst/solution systems when contrasted with gas-phase systems.

The principles of heterogeneous catalysis serve as a significant foundation for electrocatalysis; however, the primary challenge lies in addressing the distinct characteristics of electrochemical systems when integrating any relevant concepts or methodologies. A significant example of these challenges is the complex trajectory of the Sabatier principle within the realm of electrocatalysis[10]. While initially advantageous and highly effective for electrocatalytic processes, as discussed in Parsons, this principle has led to the creation of numerous "volcano plots" aimed at predicting the optimal materials—elements, alloys, or oxides—for specific electrocatalytic reactions [3]. Unfortunately, as this approach gained traction, it became counterproductive due to the excessive interpretation of these volcano plots. The Sabatier principle, along with the volcano plots, is intended to provide insights into the thermodynamic characteristics of a particular electrocatalyst based on adsorption energies, without accounting for the properties of the reaction environment. Nevertheless, these tools were frequently misapplied to fully justify the reactivity of various electrocatalysts, encompassing both thermodynamic and kinetic aspects [18].

To prevent over simplicity, it is essential to possess a comprehensive understanding of both heterogeneous catalysis and electrochemistry. The domain of heterogeneous catalysis has indeed contributed numerous prominent figures to the realm of electrocatalysis, with Elena R. Savinova [19] serving as a notable example, transitioning from heterogeneous catalysis to a diverse array of research topics within electrocatalysis.

2.2.3 Model to real electrocatalysis

From high surface to area bulk materials to single crystals and nanoparticles

A fundamental material characteristic acknowledged long before the establishment of electrocatalysis principles is the surface area of the electrode. Increasing the electrode surface area promotes higher currents at a specific potential. The first notable metallic electrocatalyst with a relatively high surface area was platinized platinum (Pt/Pt), which can be regarded as a supported dispersed catalyst. The process of plating platinum from a chloride bath for the creation of Pt/Pt electrodes is often credited to Kohlrausch in 1897, who utilized this electrode to reduce interfacial charge transfer resistance during his conductivity assessments. Nevertheless, this method was likely known prior to that time, as evidenced by references to Pt/Pt in bolometers [20]. On a microscopic level, it consists of densely coalesced small crystals, with their size, lattice distortion, preferred crystallographic orientation, and degree of coalescence being influenced by the conditions of deposition. From a modern perspective, Pt/Pt lacks a precise definition as it does not facilitate the differentiation of various structural effects in electrocatalysis.

The advancements in electrocatalyst development extend beyond metals. Electrocatalysis involving oxides has transitioned from using oxide layers on metals to the creation of chemically synthesized and more thoroughly characterized materials, where oxygen stoichiometry plays a crucial role alongside microstructure. Similarly to metals, single crystals of transition metal oxides (TMO) and oriented oxide films have been developed and employed as model surfaces to facilitate the design of more effective electrocatalytic materials. Carbon materials present an extensive variety; however, some of them present a 'well-defined' status, serving as a foundation for single- and dual-atom catalysts and enabling the production of two-dimensional (2D) catalytic materials. Additionally, numerous 2D chalcogenide catalysts have emerged, combining characteristics of both oxide and carbon electrocatalysis. These 2D materials have the potential to establish a new category of significant model electrocatalysts in the future, owing to their inherently atomically flat surfaces, although establishing a reliable electrical contact remains a challenge, typically addressed through the use of a binder for immobilization [7].

The rapid advancement of metal and metal oxide nanometer-sized catalysts has emerged the development of suitable supports to mitigate issues of agglomeration and aggregation during electrochemical processes. Essential criteria for these supports include high chemical purity, excellent electron conductivity to reduce Ohmic losses, and sufficient porosity to facilitate the effective transport of reactants to and products from the catalyst layers (CLs). Carbon blacks, such as Acetylene Black, Vulcan XC-72, and Ketjenblack, have emerged as preferred supports for industrial electrochemical applications, particularly in low-temperature fuel cells and electrolyzers, due to their ability to meet these requirements. These carbon blacks are composed of primary particles, the size of which is influenced by the production method. These primary particles aggregate to form larger structures (100–

800 nm) that further combine into loosely bound agglomerates exceeding 1 μm , resulting in a network of interconnected pores of varying sizes. By adjusting the synthetic conditions, a diverse range of carbons with distinct specific surface areas and textures can be produced for in-depth investigations of support effects, such as Sibunit carbons [21]. Research has shown that mesopores with diameters less than 50 nm within the primary carbon particles are crucial for the stabilization of metal/metal oxide nanoparticles, while larger mesopores and macropores play a pivotal role in mass transport.

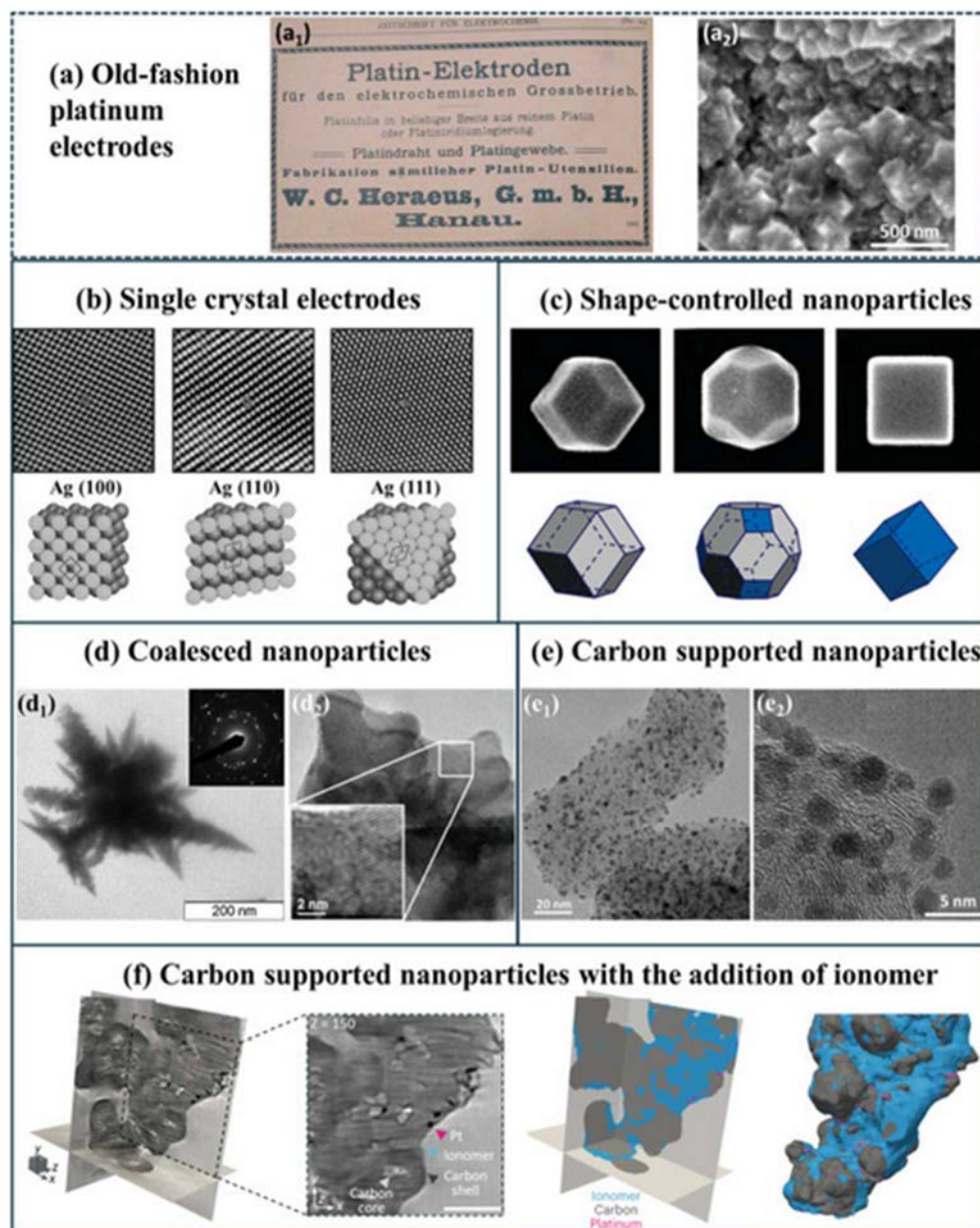


Figure 2. 1 (a) Old-fashion catalysts: advertisement of commercial Pt electrodes for large-scale electrochemical companies on the back of the issue 24 of Z. Elektrochem. 18 (1912) (a₁), along with (a₂) a typical SEM image of platinized Pt electrode; ; (b – f) Evolution of the complexity of the electrodes from single-crystal model surfaces toward catalytic layers: (b) STM images and corresponding models of three low-index faces of Ag single-crystal electrodes in 0.05 M H₂SO₄, 7 × 7 nm. ; (c) SEM images of Fe nanocrystals of a specific shape prepared by electrodeposition from a FeSO₄ + Na₂SO₄ electrolyte, and corresponding models.; (d) High resolution TEM images of electrodeposited Pt nanoparticles on (d₁) GC and (d₂) porous Vulcan XC-72 carbon highlighting complexity of the structural organization and grain boundaries, respectively. ; (e) TEM images of carbon-supported (e₁) commercial Pt/C catalyst from Tanaka and (e₂) laboratory made 5 % Pt/Sibunit catalysts with a narrow particles size distribution. ; (f) Workflow of electron tomography at cryogenic temperatures showing an analysis of Nafion–carbon–platinum aggregates with (f₁) multi-orthoslices view and (f₂) representative tomogram of a 0.7 w/w Nafion/Carbon with 8.7 wt.% Pt/C. Scale bar 50 nm; scale cube, 20³ nm³. (f₃) Segmentation results from the same aggregate and (f₄) corresponding surface rendered view[7].

Model surfaces back to real-life catalysts

Unlike model electrode surfaces, actual catalysts exhibit a multifaceted interplay of various parameters, which include the microstructure (such as surface orientation and structural defects) and the chemical composition of metal (oxide, etc.) nanoparticles, as well as the characteristics of the support material and the influence of the catalyst binder. This complexity is further compounded by the diverse range of dispersed electrocatalysts, including commercial varieties, that underpin contemporary applied electrocatalysis. Most of these practical catalytic materials are supported on external substrates, typically high surface area porous carbons, and they integrate a highly complex microstructure with an even more complex material porosity. To tackle this complexity, two primary strategies can be used. The first involves the direct examination of commercial catalysts, allowing researchers to bypass material complications and concentrate on adsorbates, reaction intermediates, and/or products. The second strategy entails systematic progression from simpler to more complex microstructures, utilizing a series of model catalysts that possess specific microstructural characteristics that mimic certain aspects of real materials. The selection of these model materials is informed by various hypotheses aimed at clarifying the reasons behind the lack of a quantitative correlation between electrocatalytic activity and the actual surface area, as measured through coulometric techniques or inert gas adsorption. The most prominent hypotheses pertain to the influences of surface crystallography, particle (or more accurately, crystallite) size, and interactions between the catalyst and its support [22]. These factors are correlated and may be specific to particular electrocatalytic reactions.

The significance of catalyst structure is demonstrated by the reaction of carbon monoxide oxidation on a platinum surface, which frequently serves as a model reaction for various fuel cell applications, such as the oxidation of organic fuels or hydrogen oxidation in the presence of carbon monoxide impurities [20]. Research using chemically deposited metal nanoparticles with a uniform particle size distribution has revealed a considerable effect of platinum particle size on the kinetics of CO adsorption and electrooxidation.

In addition to their structural attributes, the composition of metal (oxide, etc.) catalytic materials, particularly the surface composition, significantly influences electrochemical reactions. A relevant example is provided by nickel-based catalysts. Recent research has shown that variations in their surface composition, resulting from both ex-situ storage conditions and in situ treatments (such as applied potentials and electrolyte pH) before measurements, can substantially affect their electrocatalytic efficiency [7].

Toward the other face of the interface: electrolytes and ionomers

Due to its interfacial characteristics, the electrocatalytic performance is influenced not only by the structure and composition of the electrode material but also by the overall electrode-electrolyte

interface, including the properties of the electrolyte in proximity to this interface.

A striking example of this phenomenon is the influence of electrolyte pH, with H^+ or OH^- ions addressing a pivotal role in the reactions under investigation, such as the hydrogen evolution reaction (HER) and hydrogen oxidation reaction (HOR) [23]. Research has shown that the catalytic activity of platinum and other platinum group metals (PGMs) in the HER and HOR is significantly diminished in alkaline environments compared to acidic ones. This observation aligns with the understanding that both the Volmer and Heyrovsky steps of the HER and HOR are fundamentally dependent on pH, as evidenced by early experimental studies conducted on various metals. It has been suggested that the interfacial water network becomes increasingly rigid in alkaline conditions. This rigidity blocks the movement of OH^- ions toward the reaction zone at the interface, while H^+ ions exhibit greater mobility in acidic solutions. Nevertheless, the presence of hydroxides and oxides on the electrode surface may significantly influence the reactivity of interfacial water. The substantial enhancement of HER activity observed in Pt (111) modified with 3D transition metal (hydr)oxides, such as nickel, cobalt, manganese, and iron, has led to the proposal of a bifunctional mechanism for the HER, indicating that the kinetics of the reaction are influenced by both H and OH adsorption at the interface [13]. However, subsequent investigations have raised questions regarding the direct role of adsorbed OH species in the HER and HOR mechanisms.

The improvement of HER kinetics on Pt (111) in the presence of $\text{Ni}(\text{OH})_2$ is more likely due to the shift of the potential of zero total charge towards the equilibrium potential of HER/ HOR followed by a more efficient reorganization of the interfacial water. A similar effect may also be expected for the Ni/ NiO_x heterostructures [24]. It is worth noting, however, that while the hydrogen adsorption energy on Pt, the hydrogen adsorption energy appears to be only slightly affected by the presence of oxygen-containing species, the modification of the Ni surface by NiO_x species strongly impacts the energetics of the Ni-Had bond. This could explain the drastically different pH dependences of the HER/HOR kinetics observed on metallic Ni versus Ni/ NiO_x surfaces.

Both the pH and ionic strength of a solution, as well as the specific adsorption characteristics of anions and the nature of cations, can influence the kinetics of hydrogen reactions quite significantly. This phenomenon has attracted considerable attention from the researchers due to various electrocatalytic processes [7]. It was demonstrated that the so-called “spectator” electrolyte species such as solvated alkali metal cations can also substantially affect the electrode's performance due to their interaction with the surface and adsorbed intermediates. For example, it was observed that, in neutral-to-alkaline conditions, the HER rate is sensitive to near-surface concentration of cations and increases while increasing the ionic strength.

Moreover, it is important to emphasize the role of interfacial H^+/OH^- (i.e., localized pH changes, contrary to the above-discussed bulk pH effects), as its concentration is affected by the electrochemical reactions occurring at the electrode and can be considered a key determinant in

defining reaction rates and selectivity. Indeed, we have already underlined how bulk pH could impact the reactivity of an electrocatalyst. Local pH is not to be underestimated, as it may vary by several units during a given reaction [6], [25].

Incorporating an ionomer into the catalyst layer of practical catalysts, irrespective of its application within an electrochemical cell utilizing a liquid electrolyte or a reactor (for instance, in fuel cells) that employs a polymer electrolyte, further complicates the interface between the electrode and the electrolyte. Subsequently, this complexity hinders the capacity to quantitatively comprehend the interface. In a nutshell, the addition of ionomer impacts the electrocatalyst at various levels: (i) it changes the structure of the catalyst layer; (ii) it can interact with the electrocatalyst, depending on its chemical nature and the potential applied; (iii) in the absence of liquid electrolyte (as in fuel cells), it takes over a key role in ionic conductivity; in addition, its distribution determines the accessibility of active sites to gaseous reactants [26].

Nafion® is the most studied ionomer in the field of electrocatalysis, due to its well-understood molecular structure and its high ionic conductivity in an acidic environment. When used in liquid electrolyte, its main application is as a binder to ensure the structural integrity of the even more complex 3D CL [27]. The above-mentioned CLs are prepared from inks, and the ink formulation is known to affect the conformational organization of Nafion®, converting its typical rod-like morphology into aggregated particles solvated with sizes greater than 20 nm when immersed in water/2-propanol mixtures. Moreover, Nafion® can directly interact with the electrocatalyst, which occurs mainly through the SO₃⁻ groups of its side chains. It is a consensus today that its interaction with the Pt surface decreases Pt activity [28] for reactions such as the acidic ORR, with mitigation means for this phenomenon proposed both from an ionomer and an electrocatalyst engineering standpoint. A comparable phenomenon has been observed in the presence of an alkaline environment where polyaromatic ionomers, which are considered as potential alternative materials for Nafion® application to anion exchange membrane water electrolytes and fuel cells, showed that the deactivation of Pt-based electrocatalyst for HOR is highly dominated by the strong adsorption of the phenyl group on the Pt active sites.

In summary, the efficacy of a catalyst in electrochemical reactions is influenced by numerous parameters, requiring a comprehensive understanding of their effects across various levels of complexity when innovating new materials. The rapid diversification of electrocatalysts, primarily driven by the introduction of chemically synthesized nanometer-sized materials, which inevitably undergo transformations even under mild electrochemical conditions, has led to modifications in Berzelius' original concept of the catalyst. These findings have introduced a fresh perspective on electrocatalysis, a field in which the catalytic surface and its local environment are viewed as dynamic entities rather than static ones, continuously evolving under operational conditions until a steady-state composition or structure is attained. The challenge of comprehending this steady-state is further

aggravated by the intricate nature of the electrode-electrolyte interface. Thus, there is a growing need to integrate electrochemical methods with additional techniques to conduct in situ or operando experiments. During these experiments, data from spectroscopic, microscopic, or diffraction techniques are collected concurrently with electrochemical data, yielding valuable (micro)structural and compositional insights [7].

The evolution of electrocatalysis from the realm of "interfacial electrochemistry," which focuses primarily on electrochemical techniques, to that of "electrochemical surface science," which integrates both electrochemistry and surface science methodologies, is a gradual endeavor that is unlikely to reach completion soon. The primary challenge lies not in the instrumentation but in the conceptual framework: electrocatalysis functions at the interface of two intricate components, namely the electrode and the electrolyte, characterized by a potential distribution at this charged interface. This complexity at the electrode-electrolyte interface significantly impacts the transition; maintaining the integrity of this interface while merging electrocatalysis with surface science techniques remains an unfulfilled goal across numerous methodologies [7]. Nonetheless, such integration is essential. A deeper comprehension of the surface electronic states of electrocatalysts and adsorbates is vital for advancing our understanding of how electrode charge affects adsorbate reactivity and conformation. This underscores the necessity for collaboration beyond electrochemists alone; physicists with knowledge of the origins of spectroscopic responses are equally important for developing the experimental and theoretical tools required to address this complexity.

2.3 Electrochemical devices

The significant rise in global population, along with advancements in technology, are regarded as the primary contributors to the substantial increase in electrical energy consumption observed over the last fifty years. Projections indicate that global energy consumption will continue to rise, with demand anticipated to double by the mid-century and potentially triple by the century's end, driven by ongoing population growth—expected to reach 9 billion by 2048—and heightened energy requirements in industrial and commercial sectors[29]. Currently, fossil fuels, including oil, gas, and coal, dominate energy production, accounting for over 85% of the world's total energy generation. This heavy dependence on fossil fuels has resulted in various environmental issues, such as deteriorating air quality, unpredictable climate changes, contamination of water and soil, and a significant rise in greenhouse gas emissions. To mitigate or reverse these adverse effects, it is crucial to implement more sustainable, low-carbon, or even carbon-free RES, such as wind, solar, or tidal energy. However, the integration of these renewable sources poses challenges due to their location-specific and sometimes unpredictable nature, making operational flexibility essential. This flexibility can be achieved with suitable energy storage technologies, which help manage fluctuations and discrepancies between energy supply and demand, thereby enhancing the

efficiency of energy and power supply systems by narrowing the gap between production and consumption. Additionally, the increase in energy contributed to the grid through the incorporation of renewable sources like wind and solar can lead to reductions, which can be effectively managed with appropriate storage technologies [30]. A wide array of energy storage and conversion technologies is available, including chemical, thermochemical, mechanical, electrical and electrochemical storage systems options.

Electrochemistry encompasses the study of chemical processes that involve the separation of charge. This separation frequently results in charge transfer, which may occur uniformly within a solution or at the interfaces of electrodes. In practice, to maintain electroneutrality, multiple half-reactions of charge transfer occur in opposite directions. Apart from homogeneous redox reactions, these processes are spatially distinct, typically taking place at different electrodes that are submerged in a solution within a cell. These electrodes are interconnected through conductive pathways, both within the solution (via ionic transport) and externally (through electric wires, among other means), facilitating the movement of charge. If the configuration of the cell allows, the products generated from the reactions at the two electrodes can be isolated. When the cumulative change in free energy at both electrodes is negative, the electrical energy released can be utilized (as in batteries). Conversely, if the change is positive, external electrical energy can be introduced to drive electrode reactions, thereby transforming chemical substances (as seen in electrolysis) [29].

Hydrogen electrochemical devices are distinguished by their eco-friendly characteristics and superior energy conversion efficiency when compared to non-renewable energy sources such as coal and natural gas. These devices have emerged as key factors in the pursuit of sustainable energy solutions. The exhaustion of fossil fuels and the environmental damage caused by greenhouse gas emissions have prompted numerous countries to shift their attention towards the adoption of renewable energy resources. In this context, hydrogen energy is crucial, as evidenced by the European Union's objective to generate 10 million tons of hydrogen by 2030. Hydrogen can serve as an energy source in both internal combustion engines and fuel cells for electricity generation; however, its efficiency is notably greater in fuel cell applications, which significantly propels the commercialization of fuel cells. Hydrogen can be generated through various methods, including thermochemical, electrochemical, biological, and photocatalytic processes[31].

In **Figure 2.2** different types of energy storage and conversion devices are presented based on their energy delivery time varying with the type of mechanism involved in energy storage or conversion systems.

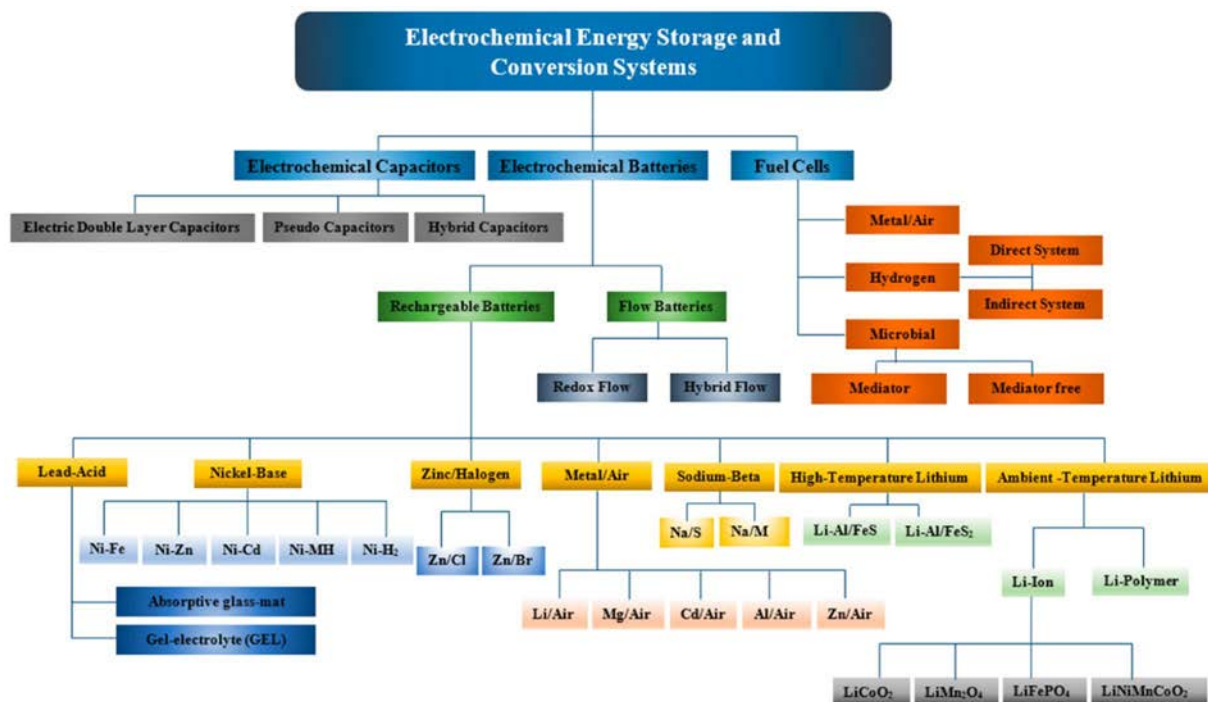


Figure 2. 2 Categories of devices for the storage and conversion of electrical energy [30].

A flow battery is composed of a negative electrode, a positive electrode, and an ion exchange membrane that serves to separate the two electrodes while facilitating the movement of ions between them. It includes two electrolyte solutions known as the anolyte and the catholyte, which participate in reversible redox reactions. These solutions are circulated into the flow battery. During the charging phase, an external power source, such as solar or wind energy, is employed to reverse the direction of the redox reactions, resulting in the oxidation of the anolyte and the reduction of the catholyte. This process effectively stores energy by isolating the oxidized and reduced species within their respective electrolyte tanks. The reverse redox reactions take place during the discharging phase, releasing the energy stored in the separated oxidized and reduced species. Then, electrons flow through an external circuit, producing electrical power. The specific chemistry of the electrolyte solutions can differ, with notable examples including vanadium redox flow batteries, zinc-bromine flow batteries, and iron-chromium flow batteries. The selection of chemistry is influenced by factors such as energy density, cost, and safety. The anolyte and catholyte solutions are maintained in separate tanks, allowing for independent scaling of the energy capacity of the flow battery, which is determined by the size of the electrolyte tanks. This capacity scaling capability is a significant advantage of flow batteries, making them ideal for large-scale energy storage applications, including grid-scale energy storage and the integration of RES. Flow batteries typically exhibit high round-trip efficiency (ranging from 70% to 85%) and an extended cycle life (up to 20,000 cycles or more), establishing them as a dependable energy storage solution [32].

Recent advances

Electrodes in a flow battery are essential for facilitating the electrochemical reactions that occur during both the charging and discharging phases. Typical materials utilized for electrodes in flow batteries include carbon-based substances such as graphite, carbon felt, and carbon paper, as well as metal and metal oxide compounds like nickel, vanadium oxide, and manganese dioxide, alongside various composite materials. Regardless of the material employed, the design of the electrodes is a key factor influencing the overall performance of the flow battery. To optimize the interaction between the electrolyte and the electrode, electrodes are frequently engineered with a high surface area, which enhances the rate of electrochemical reactions. Additionally, the integration of metal nanoparticles into the electrode material can serve as catalysts, further improving the kinetics of the redox reactions [32].

Recently, significant progress has been made in the development of membranes for flow batteries, with a focus on enhancing ionic conductivity, selectivity, and chemical stability while simultaneously lowering costs. Researchers have investigated a variety of materials, including ion-conducting polymers, composite membranes, and nanostructured membranes, all of which contribute to enhanced performance and efficiency. Innovations such as the incorporation of functionalized nanomaterials have been designed to increase permeability and minimize the crossover of active species, thereby addressing significant limitations associated with conventional membranes. These advancements are expected to enhance the competitiveness and practicality of flow battery systems in energy storage applications [29].

2.3.1 Fuel Cells

The origins of fuel cell technology date back more than 180 years to the pioneering experiments conducted by Sir William Grove, who demonstrated both the electrolyzer and fuel cell in 1839 [33]. His work led to the creation of a full-scale device, initially referred to as a gas battery, which ultimately evolved into what we now recognize as a fuel cell. The British engineer Francis Thomas Bacon is known for developing the first fully functional fuel cell in 1959, which was subsequently utilized by NASA for its space exploration initiatives [34]. During the 1960s, NASA employed both alkaline fuel cells (AFC) and polymer electrolyte membrane fuel cells (PEMFC) in missions such as Gemini and Apollo. The 1990s witnessed a surge of interest in PEMFC and direct methanol fuel cells (DMFC), driving significant advancements in the field. Today, fuel cell technology is undergoing extensive research and development, leading to technological enhancements that are paving the way for widespread commercialization. Fuel cells function as electrochemical energy conversion devices, transforming chemical energy directly into electrical energy, thereby achieving high energy conversion efficiencies. This energy conversion process occurs within the core of the cell, which consists of an electrolyte in direct contact with both the cathode (positive electrode) and anode (negative electrode). Fuel cells can be classified into six primary types based on their fuels, operating temperatures, and electrolytes [35], [36].

1. Solid oxide fuel cell (SOFC).

2. Proton exchange membrane or polymer electrolyte membrane fuel cell (PEMFC).

These can be further subdivided into standard PEMFC (operating below 100 °C) or high temperature PEMFC or HT-PEMFC (operating in temperature ranges of up to 200 °C).

3. Molten carbonate fuel cells (MCFC).

4. Alkaline fuel cell (AFC).

5. Phosphoric acid fuel cells (PAFC).

6. Direct methanol fuel cell (DMFC).

7. Single layered fuel cell (SLFC).

Fuel cell technology has been employed to a limited degree across various power applications, such as small-scale devices like personal computers and mobile phones (up to 10 kW), medium-scale applications such as transportation systems (up to 100 kW), and large-scale power applications (up to 10 MW) [37].

A fuel cell functions as a galvanic cell converting the energy from a chemical reaction, involving a continuously supplied fuel, typically hydrogen, and an oxidizing agent, usually oxygen or air, into electrical energy. Unlike conventional thermal engines, fuel cells offer the distinct advantage of directly transforming chemical energy into electrical energy, achieving higher efficiency levels ranging from about 40 **Figure 2.3** represents a schematic representation of a fuel cell.

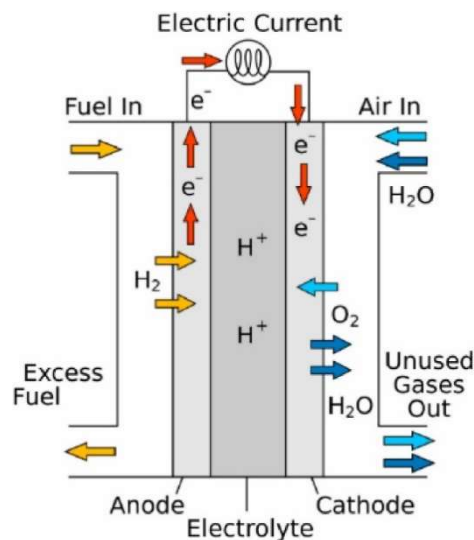


Figure 2. 3 Schematic of fuel cells[38].

Fuel cells are highly efficient (almost three times greater than the internal combustion engines) and because they do not have moving parts, they do not need to be repaired or replaced. Fuel cells have various applications such as submarines, spaceships, airplanes, and cars.

Fuel cells represent a technology for energy conversion that transforms chemical energy into electrical energy through electrochemical reactions. This process generates electricity directly

from the oxidation of fuel, eliminating the need for thermodynamic conversion. As a result, fuel cells achieve high efficiency in energy conversion and produce no pollutants associated with combustion reactions. Typically, hydrogen serves as fuel, which is supplied to the anode side for oxidation, while an oxidizing agent, usually air or pure oxygen, is introduced to the cathode side. The flow of electrons through an external circuit generates an electric current, accompanied by ion exchange facilitated by electrolytes within the cell. A redox reaction takes place, yielding water and heat as by-products. These cells can be assembled in stacks, with interconnecting plates providing positive and negative connections, along with the end plates that ensure compression and optimal contact among the components [39].

A key difference between fuel cells and batteries is their approach to energy storage and production. Batteries rely on the quantity of reactants to store and generate energy, while fuel cells can continue to function if fuel is available, with decreased operation only due to component degradation, as is typical and expected of such systems. To scale up fuel cell operations, it is generally necessary to increase the number of stacks, and the power density is contingent upon the active area of the cells, with typical output per unit surface area ranging from 0.1 to 2.5 W/cm². As fuel cells generate direct current (DC), they require a power conditioner to convert this to alternating current (AC), which results in some power losses during the conversion. One of the most important advantages of fuel cells is their ability to respond to load variations while maintaining efficiency at partial loads, with typical efficiencies falling between 40% and 60%, and electricity generation that is largely unaffected by the size of the cell [40].

Additionally, the heat generated by fuel cells can be used for cogeneration applications or for further electricity generation through thermodynamic cycles.

Various fuel cell types have been developed to satisfy various application requirements. These cells are classified based on the electrolyte type, with operating temperatures and the ions transported being essential factors influencing their applications. Electrolytes can be categorized into several categories: liquids at ambient temperature and pressure, electrolytic solutions, polymeric membranes that generally need high humidification, pure or mixed molten salts, solid oxides, and proton-conducting ceramics, where the lattice structure is crucial in determining conduction temperatures and the ions transported. Based on their electrolyte type, fuel cells are classified, with proton exchange membrane fuel cells (PEMFCs), alkaline fuel cells (AFCs), phosphoric acid fuel cells (PAFCs), direct methanol fuel cells (DMFCs), molten carbonate fuel cells (MCFCs), and solid oxide fuel cells (SOFCs). Among these, MCFCs and SOFCs operate at high temperatures (600 to 1000 °C), PAFCs operate at medium temperatures (175 to 200 °C), while AFCs, PEMFCs, and DMFCs operate at lower temperatures (70 to 120 °C). It is important to note that DMFCs are a subset of PEMFCs, using methanol as a fuel source instead of hydrogen. The primary benefit of operating PEMFCs at lower temperatures is their rapid start-up capability.

Conversely, operating at higher temperatures (approximately 200 °C) offers several advantages, including improved heat recovery potential, prevention of water accumulation at the cathode, enhanced tolerance of the platinum catalyst to impurities such as carbon monoxide, thereby allowing for a broader range of fuels sources, and an overall increase in cell efficiency [39].

The presence of carbon monoxide (CO) and carbon dioxide (CO₂) as contaminants in the fuel or air supply for low-temperature fuel cells presents significant challenges. These contaminants can bind with catalysts or electrolytes, leading to catalyst degradation and necessitating the use of costly CO₂ scrubbers. This issue is particularly critical for alkaline fuel cells (AFCs) and for the slow anode electrocatalysis of methanol in direct methanol fuel cells (DMFCs). It is important to highlight that proton exchange membrane fuel cells (PEMFCs) are the most extensively studied type of fuel cell, as evidenced by the literature reviewed in this thesis. Advances in design, membrane electrode assemblies, lightweight stacks, thermal management, and overall technology have made PEMFCs one of the preferred options for commercial applications. A critical consideration for PEMFCs, and fuel cells in general, is their water management; dehydration can lead to cell failure, while overhydration can reduce efficiency by impeding the transport of reactive species. In contrast, phosphoric acid fuel cells (PAFCs) exhibit greater tolerance to CO and CO₂ compared to AFCs and PEMFCs. While many fuel cells require reformers or other mechanisms for hydrogen production, molten carbonate fuel cells (MCFCs) can internally reform and are less sensitive to impurities such as CO and CO₂. However, MCFCs are economically viable for large-scale operations exceeding 100 kW, with a 59 MW facility currently supplying power to a city in South Korea. Despite their advantages MCFCs face several challenges, including high costs for smaller-scale operations, corrosive electrolytes, gradual electrolyte loss, and cathode dissolution. Solid oxide fuel cells (SOFCs) offer additional advantages, particularly in combined heat and power applications or in hybrid cycles with gas turbines, leading to highly efficient electricity generation. Among the fuel technologies, SOFCs are recognized for achieving the highest efficiency [40].

The cell potential is specified by calculating the potential difference between the anodic and cathodic electrodes, as presented in the following equation. The resulting value is measured in volts (V), as shown in the next **Equation 1**.

$$E_{cell}^0 = E_{catho}^0 - E_{anode}^0 \quad (1 \text{ M and } 1 \text{ bar}) \quad (\text{Equation 1})$$

If the standard circumstances are altered, the Nernst equation can be used as a guideline to calculate:

$$E = E^0 - \frac{RT}{nF} \ln Q \quad (\text{Equation 2})$$

which is derived from Gibbs free energy in next equation

$$\Delta G^0 = -nFE^0 = \Delta H^0 - T\Delta S \quad (\text{Equation 3})$$

This is calculated using the balanced reaction equation and thermodynamic tables. When ΔG is positive, it implies the reaction demands external energy (nonspontaneous reaction), while when it is negative, the reaction may take place in the absence of external energy (spontaneous reaction) [41], [42].

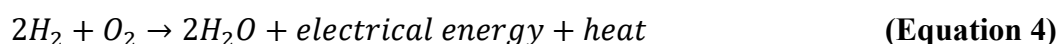
Advantages VS disadvantages of fuel cells

As advantages, fuel cells operate outside the constraints of the Carnot cycle, resulting in significantly higher efficiency compared to heat engines, typically ranging from 40% to 60%. When the heat generated by fuel cells is utilized, their efficiency can reach approximately 90%. Additionally, fuel cells are devoid of moving components, which eliminates the need for part replacements. They are environmentally friendly, operate quietly, and can be conveniently installed in various locations. Currently, 20% of electricity generated in power plants is lost during transmission to end users; however, fuel cells mitigate this issue, thereby minimizing electricity loss. The primary fuel for fuel cells is hydrogen, which can be derived from the electrolysis of water, methanol, and other hydrocarbon sources, making fuel cells adaptable in terms of fuel options [43].

On the other hand, the reaction proceeds at a low rate, which consequently results in low power and current outputs. The availability of hydrogen as a fuel is also quite limited. Additionally, this technology is not well-known internationally. The high expense of the necessary equipment has further impeded the widespread availability of this technology [40].

2.3.2 How a fuel cell works

Within a fuel cell, oxygen is inserted in the cathode and hydrogen into the anode. During the procedure, a hydrogen atom loses an electron and becomes a hydrogen ion (H^+). In order to permit only the passage of hydrogen ions, electrolytes are used, while electrons are directed to the cathode through the output junction, avoiding the electrolyte. At the cathode, these electrons are utilized by oxygen, facilitating the reduction of oxygen ions. The hydrogen ions that traverse the electrolyte then react with oxygen ions (O^{2-}), leading to the production of water, which is subsequently eliminated from the system as a secondary product. This reaction can be characterized as the inverse process of water decomposition.



The operational principles of fuel cells exhibit similarities across different types. In low-temperature fuel cells, a buffer is situated between the two reactants, namely protons and oxygen. The specific characteristics and type of buffer are crucial for the electrochemical efficiency of the fuel cell. In these systems, the reactive gases diffuse through a thin electrolyte layer, facilitating the chemical reaction at the respective electrode surfaces. If the pores of the electrode are blocked by an overabundance of electrolyte, the movement of ions within the electrolyte phase toward the

reaction site is hindered, resulting in a reduction of the electrode's chemical efficiency. Consequently, it is imperative to maintain an accurate equilibrium among the electrode, electrolyte, and gases within the electrode pores. In high-temperature fuel cells, the separation between the electrodes consists of a thin electrolyte layer. This electrolyte not only serves as an ionic conductor between the electrodes but also acts as a barrier to ensure that the flow of fuel and oxidant remains directed along the intended path [34].

2.3.3 Types of fuel cells

Fuel cells are categorized as follows: Alkaline fuel cell, phosphoric acid fuel cell, molten carbonate fuel cell, polymer fuel cell and solid oxide fuel cell. **Table 2.1** summarizes the different types of fuel cells.

Table 2. 1 Categories of fuel cells based on electrolyte [43] .

Types of cells	alkaline	Methanolic	Molten carbonate	phosphoric	polymeric	Solid oxide
Electrolyte	Potassium hydroxide	Polymer membrane	Molten carbonate	Phosphoric acid	Replacement membrane	ceramic
Operating temperature	60–90	60–130	650	200	80	100
Yield (%)	40–60	40	45–60	35–40	40–60	50–65
Production power	Up to 20 kW	Less than 10 kW	More than one kilowatt	More than 50 kW	up to 25 kW	More than 200 kW
Application	Submarine, Space	Portable applications	power plant	power plant	Vehicles, power plant	power plant

2.3.4 Alkaline fuel cells

Alkaline fuel cells (AFC) are among the revolutionary technologies in the field of fuel cells, predominantly employed to produce electrical energy and water in space missions. In these systems, a potassium hydroxide solution dissolved in water acts as the electrolyte, and it can also function as a catalyst at both the anode and cathode, unlike more economical metal options. High-temperature AFCs operate at temperatures ranging from 100 °C to 250 °C, whereas innovative AFC designs are being developed to function at lower temperatures, specifically around 23 °C to 70 °C [44].

Advantages VS disadvantages of alkaline fuel cell

A critical concern regarding these batteries is their vulnerability to impurities of carbon oxides in the fuel, which results in the creation of potassium carbonate and greatly limits their performance. Furthermore, it is essential to note that the water generated at the anode is twice that which is consumed at the cathode, thus necessitating continuous removal [44].

2.3.5 Phosphoric acid fuel cells

In 1961, novel types of fuel cells known as intermediate temperature cells was introduced. During the testing phase, an electrolyte consisting of 35% phosphoric acid was utilized in place of the traditional sulfuric acid electrolyte battery. The battery experiences electrochemical depletion while the system is in operation. Presently, phosphoric acid fuel cells have reached commercial viability. The losses attributed to cathode activation polarization are significant when compared to the negligible effects of concentration polarization, anode activation polarization, and ohmic polarization. These fuel cells operate at temperatures ranging from approximately 150 to 200 °C. Positive hydrogen ions migrate from the anode to the cathode through the electrolyte, where they combine oxygen ions and electrons to form water, which is then expelled from the battery. The incorporation of a platinum catalyst in the electrodes enhances the reaction rates within the battery. However, due to the limited conductivity of phosphoric acid, the development of these batteries has been somewhat constrained [45].

Advantages VS disadvantages of phosphoric acid fuel cells

In contrast to alkaline fuel cells, these batteries can use CO₂ and CO as fuels. Thus, the fuel sources for these batteries may include natural gas (methane), petroleum derivatives (such as naphtha), coal-derived liquids (like methanol), or gases produced from coal. The operational temperature of these batteries is relatively moderate, allowing the waste heat generated by the system to be harnessed for environmental heating. To enhance the battery's efficiency, the incorporation of noble metals as electrocatalysts is essential. However, an increase in the concentration of carbon monoxide within the system can lead to battery poisoning, thereby diminishing its efficiency [46].

2.3.6 Molten carbonate

A molten carbonated fuel cell is characterized by its high operating temperature, serving as an effective energy conversion device. The significant heat generated by these cells can be harnessed for environmental heating or for the generation of supplementary electricity. In the process, hydrogen at the anode interacts with carbonate ions, yielding water and carbon dioxide. Meanwhile, the carbonate ions produced at the cathode are transferred into the electrolyte. This fuel cell technology is versatile, using fuels such as heavy hydrocarbons, methanol, and natural gas [47].

2.3.7 Polymer fuel cells

The development of this battery begins in the early 1960s, initiated by the General Electric Company for the United States Army. The energy source for this battery is derived from hydrogen, which is generated through the reaction of water and lithium hydride. These batteries exhibit efficiency ranging from 40% to 50%. In polymer fuel cells, a very thin, permeable polymer membrane serves as the electrolyte. This membrane is not only thin and transparent but also operates at approximately 80 °C. To enhance the rate of reactions, a platinum catalyst is applied to both sides of the membrane. At the anode, hydrogen atoms undergo ionization by losing electrons and subsequently diffuse through the membrane's pores toward the cathode. At the cathode, the electrons and protons from hydrogen, along with air or oxygen molecules, react to produce water [45].

The operational mechanism of a polymer electrolyte membrane fuel cell (PEMFC) resembles that of other types of fuel cells. Its configuration includes a gas diffusion layer (GDL), a polymer electrolyte membrane (PEM), a bipolar plate, and a catalyst layer (CL), as illustrated in **Figure 2.4**.

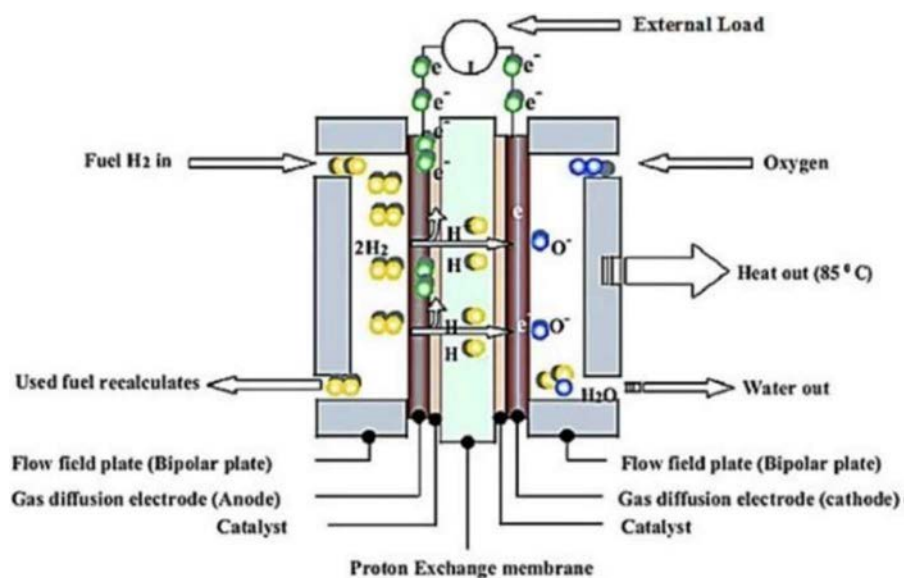


Figure 2. 4 Schematic of working principle of PEMFC [43]

Advantages VS disadvantages of polymer fuel cells

The durability of the electrolyte ensures that there is no displacement or evaporation of the electrolyte from the system. As a result, water remains the only liquid in the system, which contributes to reduced corrosion. Furthermore, the battery is characterized by a short start-up duration. Nevertheless, it is crucial for the battery to function in a manner that prevents the water produced from the reaction from dissipating into the air faster than it is formed. This condition limits the operational efficiency of the battery to temperatures below 60 °C. Additionally, the presence of even a minor amount of carbon monoxide can lead to the poisoning of the catalyst on its electrodes [46].

2.3.8 Solid oxide fuel cells (SOFCs)

Solid oxide fuel cells (SOFCs) are fundamentally different from other fuel cell technologies, as they are solid-state devices that lack moving parts. They possess unique features, including operation without combustion, minimal emissions, high conversion efficiencies, and the ability to function at elevated temperatures ranging from 800 to 1000 °C. Recent initiatives have focused on the development of novel electrode materials aimed at enhancing their thermal stability, electrical conductivity, catalytic performance, chemical compatibility, and cost-effectiveness, particularly in light of the reduction in operational temperature from 400 °C to 700 °C [48], [49].

SOFCs represent the pinnacle of efficiency in the direct conversion of chemical energy into electrical energy. The foundational concept of this technology was introduced by Nernst and his associates in the late 19th century. It is important to acknowledge that significant advancements in both the theoretical and experimental aspects of this technology have occurred over the past century. **Figure 2. 6** represents the schematic representation of a solid oxide fuel cell. This system utilizes a solid electrolyte composed of ceramic material, specifically zirconia stabilized with yttria (YSZ). Within the temperature range of 600 to 1000 °C, this material functions as an ionic conductor, facilitating the reduction of oxygen atoms by electrons on the porous surface of the cathode. This process results in the formation of oxide ions, which then migrate through the ceramic body to the anode, where fuel is abundant. At the anode, these oxide ions react with hydrogen, acquiring the outer orbital electrons. A total of five components are required to construct a battery: the electrolyte, anode, cathode, and two connecting wires [50].

The selection of appropriate anode materials is crucial for ensuring the optimal performance of SOFCs, as these materials constitute approximately 95% of the total material composition in anode-supported cells. The most prevalent anode material utilized in SOFCs is Ni-YSZ, recognized for its remarkable stability and excellent conductivity. However, it is susceptible to carbon deposition when exposed to hydrocarbon fuels. Research conducted by Song et al. demonstrated that the performance of Ni-YSZ-based SOFCs could be enhanced by doping the anode with Al_2O_3 , which led to improved electrical conductivity, reduced anode activation polarization, and an impressive 39% increase in cell performance. Other anode materials employed in SOFCs are CrTi_2O_5 , Cu-CeO_2 , $\text{La}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.8}\text{Cr}_{0.2}\text{O}_3$, and $\text{Sc}_{0.1}\text{Y}_{0.1}\text{Zr}_{0.6}\text{Ti}_{0.2}\text{O}_{1.9}$ [51].

The cathode serves as a crucial element within a solid oxide fuel cell (SOFC) system, distinguished by selection criteria that differ from those of the anode. This distinction arises from the cathode's requirement for specific operational characteristics, including a high degree of porosity and stability in an oxygen-rich environment. Furthermore, due to the elevated temperatures at which SOFCs operate, they utilize more economical and readily available transition metal oxides, such as copper, cobalt, cerium, strontium, and nickel, as alternatives to more expensive metals like platinum. The high-temperature conditions enhance the kinetics and

thermodynamics of the chemical reactions essential for fuel cell functionality. Additionally, SOFCs can function as alternatives to electrochemical batteries, demonstrating high efficiencies even in reverse mode as solid oxide electrolysis cells (SOEC) [52]. In this mode, steam is electrolyzed into hydrogen by introducing water and electric current into the cell, yielding hydrogen and oxygen. Given these advantageous properties, along with their modularity, fuel adaptability, and suitability for various scales of application—ranging from small to large—and their vibration-free, quiet operation, SOFCs represent promising candidates for future energy storage and conversion technologies [53].

The fuel cell embodies a unique elegance and simplicity, making it surprising that this technology has not yet been adopted for commercial use. Should this technology be commercialized, it has the potential to replace combustion engines, thereby significantly reducing urban pollution. A considerable factor contributing to the current limitations in this field is the insufficient understanding of materials and the engineering expertise necessary for advancing electrochemical technology. However, it is our belief that advancements in knowledge and skills are progressing rapidly. A critical element in the design and utilization of SOFCs is the heat generated from chemical reactions. The heat leads to ohmic losses and electrodes' overvoltage within the battery. Such losses are inherent in all designs and cannot be eliminated; instead, they must be managed through an effective thermal management system. In fact, maintaining the battery's operating temperature relies heavily on this heat. The primary advantage of solid oxide fuel cells over other fuel cell types is the high temperature of the heat output, which simplifies control and enhances cost-effectiveness [49], [52]. Given that both electricity and heat are valuable outputs of solid oxide fuel cells, optimal applications are those that leverage both. For instance, local combined heat and power systems can utilize auxiliary power for devices, while fixed power generated from coal is well-suited for the gasification process. An auxiliary solid oxide fuel cell system can harness this heat to produce hot water, a function currently performed by basic converters. Additionally, this heat can be employed to maintain warmth for the driver in a vehicle. A consistent power generation system can utilize the hot exhaust gases from a solid oxide fuel cell to facilitate coal gasification or to operate a heat engine or gas turbine engine [54].

The aforementioned were first proposed over a century ago. In 1890, the concept of electrical conductivity was not well understood, as the electron had yet to be identified. Metals were deemed conductive in accordance with Ohm's law, while ionic conductive solutions were recognized for their ionic conductivity. Nernst later made pioneering observations regarding the different forms of conductivity in zirconia that had been stabilized with materials such as calcium oxide, magnesium oxide, and yttrium oxide. He discovered that zirconia, when stabilized at room temperature, functions as an insulator, and that the ions of the conductive agent enable conduction at high temperatures between 600 and 1000 °C, with ionic conduction conditions occurring at approximately 1500 °C [12]. He subsequently filed a patent for a zirconium filament used in

electric light bulb production, marketing his invention by claiming its application in his home lighting system.

Zirconium films were unable to effectively compete with tungsten films, resulting in the discontinuation of Nernst's invention until the 1930s, when a laboratory-scale proposal for fuel cells based on zirconium oxide emerged. Baur and Peris managed to create this fuel cell in a laboratory environment, utilizing a crucible composed of stabilized zirconia with 15% yttria as the electrode, while magnetite (Fe_3O_4) was employed as the anode [12]. The cathode contained either H or CO, with air serving as the oxidizing agent. By connecting eight cells in series, they developed the first fuel cell capable of producing electricity, which indicated the potential for this type of battery to compete with others. Nevertheless, several challenges had to be addressed before this could be achieved, particularly the need to optimize the electrolyte production process, which was still in its early stages. Reducing the cell's resistance from [55].

The low power density required the implementation of an array of batteries. Significant attention was needed in areas such as establishing link between numerous cells, understanding the dynamics of fuel reactions, and ensuring the proper functioning of the system. During the 1950s, experimental studies focused on pressed or cast disks of yttria-stabilized zirconia, leading to the development of a straightforward design for experimental systems that remain in use today. These cells necessitate a flat disk of yttria-stabilized zirconia, with an anode and cathode on either side, all enclosed within a ceramic tube. This sealed configuration is subjected to high temperatures within a furnace. A smaller tube is inserted into the ceramic tube to deliver fuel to the anode, while another tube supplies oxidizing gases to the cathode. Current collector wires and voltage measuring probes are removed from the surfaces of the electrodes. Previously, a flat sheet of electrolyte was employed, illustrating how the voltaic aspect of this flat plate can be formed from distinct, internally connected plates, thereby creating a functional reactor [12].

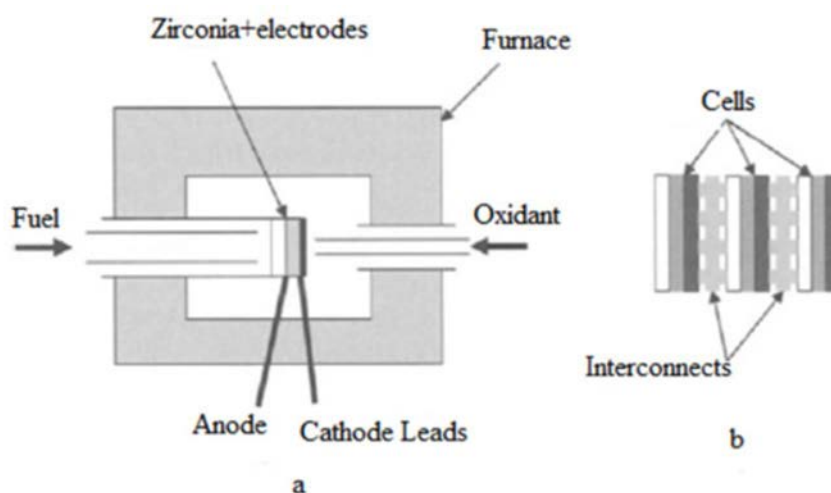


Figure 2. 5. Sequence of cells [38].

It is essential for plates with internal connections to comprise an anodic current collector

and a cathodic current collector, which are unified within a single plate, resulting in the formation of two components. Moreover, these internal connectors can feature gas channels that transport fuel to the anode and the oxidizing agent to the cathode. They also serve to connect the cathode of one cell with the anode of another [56].

It has been determined that numerous issues exist within the domain of interconnected page components. To generate increased power, the surface area of these components must be enlarged, which necessitates an expansion of the sealing areas along the edges as well. This enlargement leads to discrepancies in the coefficients of thermal expansion among the components, resulting in the formation of cracks. Consequently, tubular designs have gained significant success in recent years, with this configuration being produced in substantial quantities [50].

A SOFC is now a standard component in every vehicle. SOFC functions as an oxygen sensor, which is integrated within the exhaust manifold. It regulates the oxygen levels in the exhaust fluid that flows into the exhaust catalyst. Maintaining the chemical composition of this fluid close to a stoichiometric ratio is essential for the catalyst to operate at its peak efficiency [50]. Typically, yttria-stabilized zirconia (YSZ) is utilized as an electrode due to its effective oxygen detection capabilities. The surface of this ceramic material is generally coated with platinum using specialized inks. The initial design, which dates to the 1970s, bore similarities to the configurations developed by Baur and Preis. A YSZ tube containing 8% yttria was pressed and sintered at a temperature of 1500 °C to achieve the desired density. Platinum electrodes were then applied, followed by the placement of a steel cap, which was installed within the exhaust manifold, allowing the YSZ and anode to be exposed to the hot gases. Air was introduced to the cathode surface to serve as an oxygen reference. A wired connection facilitated the transmission of voltage from the internal electrodes to the energy management system, while the other electrode was integrated into the vehicle's chassis. When the exhaust temperature exceeded 600 °C, the voltage generated by this system indicated oxygen concentration, leading to the designation of this sensor as the Landa sensor [57].

The control system uses the signals from the oxygen sensor to optimize engine performance, thereby ensuring the ideal mixture is delivered to the catalyst. Over the years, numerous enhancements have been made to this fundamental system. For instance, a heating element can be incorporated within the ceramic cylinder to expedite sensor heating. A significant modification was introduced in 1997 by Robert Bosch [58], who reengineered the zirconia sensor using an alternative manufacturing process. Instead of forming a ceramic tube from dry powder, a mixture of zirconia powder was combined with polymer additives and applied in a manner akin to paint, utilizing a moving strip.

This procedure bears resemblance to the manufacturing process of ceramic capacitors utilized within the electronic ceramics sector. The new device presents several advantages, including:

- A reduced quantity of zirconia utilized in its fabrication.
- A thinner ceramic electrolyte that enhances response time.

- The capability to easily print heaters and other circuits on flat surfaces.

A notable benefit of this technology is the ability to create sensors with a linear response, as opposed to the logarithmic response characteristic of tubular sensors, thereby facilitating a more straightforward adaptation of the electrical control system. This is achieved by establishing the oxygen reference on one of the surfaces, functioning as an oxygen pump. The reference oxygen can subsequently be expelled through a standard aperture in the cathode structure. Currently, oxygen sensors find extensive application in oxygen storage, metal processing, and flame control, with the automotive industry representing the largest market for this technology [59]. The commercialization of zirconia technology for sensors has significantly propelled the advancement of materials employed in fuel cells. The primary distinction lies in the fact that these sensors operate at such low power levels that only partially stabilized zirconia is applicable. In contrast, fully stabilized zirconia is required for high power applications to ensure the longevity of the electrolyte [12].

Nowadays, the predominant electrolyte materials utilized in solid oxide batteries are yttria-stabilized zirconia. While other oxide materials also exhibit ionic conductivity, with some demonstrating superior conductivity, yttria-stabilized zirconia possesses distinctive characteristics that have facilitated its application in this field. These characteristics include its high availability, chemical stability, non-toxicity, and cost-effectiveness. However, there are certain drawbacks associated with this material, such as high thermal expansion coefficient, challenges in forming connections, and sealing issues. Currently, low-grade stabilized zirconia enjoys a robust market, particularly in refractory applications, pigmented coatings, and pottery colors. Nevertheless, it is only in recent years that higher quality zirconias have been developed for use such as thermal barrier coatings on gas turbine components, hip implants, and cutting tools. Much of this technological advancement has stemmed from research into pure zirconia and the influence of minor dopants on its crystal structure and properties. In 1970, the annual production of this material was limited, and its cost was relatively high. However, the introduction of Landai zirconia sensors for monitoring automotive exhaust gases in the 1970s led to an increase in production and a subsequent reduction in price. By 2000, the cost of this material was about \$50 per kilogram, with projections indicating a decrease to around \$13 per kilogram by 2020, coinciding with an annual production reaching thousands of tons. In 2000, the global consumption of YSZ sensors was estimated at about 500 tons, but it is anticipated that the demand for YSZ in SOFC systems will surpass that of sensors by around 2010 [50].

It remains uncertain whether substantial quantities of zirconia will be utilized in SOFC applications soon. Conversely, the application of titania has seen a notable increase over the past century, particularly in color-related uses. Fortunately, zirconia is one of the more abundant materials found in the Earth's crust, with its prevalence surpassing that of copper and zinc, for instance. Significant deposits of zirconia can be found across Australia, Africa, Asia, and the

Americas, where it typically occurs as a silicate mineral. The silicate form of zirconium is referred to as zircon. A primary challenge in terms of cost lies in the purification of this mineral, particularly in the separation of silica, which tends to obstruct ion and electron pathways within fuel cell systems. For electrolytic applications, an appropriate zirconia powder should contain less than 0.1% silica by weight. Other impurities, such as alumina and titania, which can release silica, are generally acceptable at around 0.1% by weight. Hafnia is the principal impurity found in zirconia, typically present at a few percent by weight, but it does not pose significant issues, as it is also recognized as an ion-conductive material [60]. Zirconia may contain trace amounts of impurities that emit harmful alpha radiation, which could lead to health concerns during handling; however, there are no other notable toxic substances associated with this material. Presently, yttria is the preferred stabilizer, despite being more costly than scandium and ytterbium oxides, due to its superior conductivity [61]. For instance, yttria is commonly added to zirconia at approximately 13–16% by weight (8–10.5% mol) to ensure the stability of the cubic phase [56]. The introduction of traced dopants such as scandium oxide may present challenges in the future. Nonetheless, a significant hurdle remains in transforming electrolyte materials into devices with specific functionalities, as the production of high-quality electrolytes is one of the primary concerns in the advancement of SOFC. The success of an electrolyte is contingent upon its ability to fulfill various important criteria, such as [26]:

- Economical material
- Resistant material
- Thin material for little ionic resistance
- Appropriate composition of material for ionic conductivity at the temperature of operate
- Material with ability to release air

Meeting these requirements poses significant challenges. Historically, industrial ceramic processes have relied on dry pressing techniques utilizing either metal or rubber molds. While zirconia sensors have been produced through these methods and are commonly employed in academic research, achieving thin walls of zirconia remains problematic. In the 1960s, a tube design was introduced that utilized the dry pressing technique; however, this approach proved costly due to the necessity of using diamond-abrasive materials for thinning the electrolyte. It appears more advantageous to explore advanced ceramic production techniques, such as chemical vapor deposition and strip casting or extruding methods, to effectively create thin electrolyte layers [56].

During the late 1970s, Westinghouse [62], an electronics manufacturer, employed the vapor deposition technique to fabricate tubular cells. A porous, tube-shaped substrate, measuring 15–20 μm in diameter, was positioned within the chamber of a low-pressure furnace. Initially, this substrate was composed of zirconia stabilized with calcium oxide, but it was later made from a doped cathode material, specifically lanthanum magnetite. Zirconium chloride and yttrium chloride vapors were

introduced through the outer section of the tube, resulting in the formation of a 40- μm thick layer on the substrate's surface, which ultimately became the electrolyte layer. Additionally, a connecting strip could be produced using lanthanum chromate doped with magnesium oxide through the same method [61]. Despite the favorable electrochemical performance of tubular solid oxide fuel cells, this process is more time-consuming and costly compared to the strip casting method. Furthermore, large pipes require a prolonged heating period, necessitating preheating for 4–6 hours. Strip casting is predominantly utilized for creating thin material layers in electronic applications, particularly with organic solvents. A slurry of YSZ powder is prepared using dispersing agents and solvents, such as methyl ethyl ketone or ethanol combined with KD1. This slurry undergoes grinding in a ball mill for 24 hours to ensure proper consistency and to break down any lumps. Subsequently, a mixture of plasticizer and polymer material, derived from grinding polyethylene and dibutyl phthalate oxides with a solvent, is incorporated into the slurry. After filtering and eliminating air from the mixture, the slurry is cast onto a polymer layer and dried for three hours before being baked at 1300 °C. Due to environmental considerations, water-based tape casting is preferred over organic solvent-based methods. Viking Chemical pioneered the development of water-based strip casting, producing pure zirconia through solvent extraction techniques [63].

In this approach, the calcined zirconia powder undergoes abrasion in an aqueous medium containing ammonium polyacrylate solution, resulting in a slurry with optimal dispersion. Subsequently, a solution of pure ethylene cellulose is incorporated into this mixture, followed by a process of filtration and aeration. The resulting slurry is then cast onto a polymer film, after which it is dried and subjected to baking at a temperature of 1450 °C. A significant challenge in flat structures is the emergence of thermal inconsistencies. To mitigate these issues, it is essential to gradually heat the samples. Additionally, pipes with a smaller diameter are fabricated using the extrusion method to further address thermal inconsistencies. When producing zirconia membrane, it is crucial to establish electrodes on the contact surface of the fuel (anode) and the oxidizing material (cathode). These electrodes are typically formed from particulate materials that are partially sintered to create a porous conductive layer. Often, multiple layers are developed to achieve a gradient of properties, with pure YSZ at the electrolyte surface and a material matching the chemical composition of the electrodes at the contact interface. This approach also allows for better adaptation of thermal expansion coefficients [61].

The most frequently employed material for anodes in solid oxide fuel cells is nickel, largely due to its recognized performance and economic advantages. Nonetheless, nickel does not bond effectively with YSZ, resulting in crust formation unless it is blended with zirconia. This issue of flaking is attributed to the considerable difference in thermal expansion coefficients, with nickel measuring $13.3 \times 10^{-6} \text{ K}^{-1}$ and YSZ approximately $11 \times 10^{-6} \text{ K}^{-1}$. By mixing 30 percent by volume of nickel oxide with YSZ and baking the mixture at 1300 °C, a porous anodic layer is produced through hydrogen reduction, which alleviates the thermal expansion mismatch. The thermal expansion coefficient of this nickel cermet

anode is about $12.5 \times 10^{-6} \text{ K}^{-1}$, which improves its adhesion to YSZ. Additionally, by sandwiching this anode between two materials with slightly different chemical compositions—one closer to zirconia with lower nickel content and the other more aligned with the gas flow containing higher nickel content—enhanced anode characteristics can be realized. The essential criteria for an effective anode include facilitating rapid and efficient reactions, ensuring proper fuel interaction, and maintaining adequate conductivity at the junction [61].

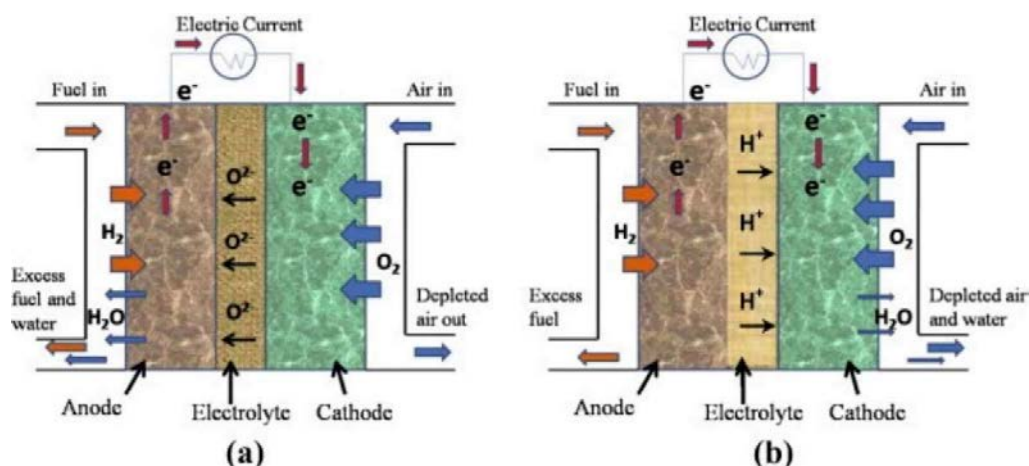


Figure 2. 6 Schematic representation of solid oxide fuel cell (SOFC) (a) oxide-ion conducting electrolyte, (b) proton conducting electrolyte [11].

A SOFC is fundamentally composed of a porous anode and cathode that are positioned around a ceramic-based solid electrolyte, which may include materials such as yttria-stabilized zirconia (YSZ) or gadolinium-doped ceria (GDC), as illustrated in **Figure 2. 6**. Over the past three decades, materials engineers have encountered significant challenges in the design of these cells. The power output of these cells is directly proportional to the cell area, necessitating that the maximum area of the YSZ membrane be incorporated within the fuel cell [61]. This challenge parallels issues faced in the design of heat exchangers. Two viable solutions include the arrangement of flat plates or the use of an array of parallel tubes. Similar design challenges, such as cracking, inadequate sealing, and gas leakage, are also present in these fuel cells, primarily due to the use of diverse materials with high thermal expansion coefficients. These issues are exacerbated by the elevated operating temperatures of the devices. Additional complications arise from the low toughness of ceramic components and the requirement for conductive connections among all cells. Plate cells offer distinct advantages, as they can be easily subjected to stencil printing, allowing for minimal spacing between plates and the achievement of high-power densities. Furthermore, establishing connections between these plates is relatively straightforward [55].

SOFC technology possesses the capability to significantly alter the landscape of electrical energy generation with minimal environmental repercussions, provided it is commercialized on a larger scale. However, its commercialization has been hindered by various challenges, including elevated material costs, the necessity for high operating temperatures ranging from 800 to 1000 °C, safety concerns, and the intricate nature of stack and cell assembly. Additionally, the high operating

temperatures introduce further complications such as catalyst poisoning, electrode sintering, interfacial diffusion between electrodes and electrolytes, and issues related to thermal and mechanical stability. These challenges, particularly the requirement for elevated operating temperatures, have prompted research efforts to explore low-temperature SOFC technology. The advantages of reducing operating temperatures encompass an expanded range of applications, enhanced longevity of SOFCs, technical advancements (such as minimizing the risk of redox degradation in cermet anodes), and economic benefits through the utilization of more cost-effective cell components [11].

Numerous companies engaged in the production of solid oxide fuel cells currently employ plate design, primarily due to the aforementioned advantages. However, two significant challenges persist: one persists in heating, while the other concerns the serving of these devices. The slow heating associated with the plate design, along with the sealing issue, arises from the high coefficient of thermal expansion of YSZ and its inherent brittleness. Rapidly heating a plate array of a fuel cell to a temperature of 800 °C may result in cracking, leading to potential failure. This challenge is common to all large YSZ structures. Consequently, it is essential to utilize smaller YSZ plates or tubes to mitigate thermal shock. However, this adaptation results in an increase in the overall size of the cell design. In power generation systems utilizing solid oxide fuel cells, for instance, cell components constitute approximately 25% of the total volume of the fuel cell system. The remaining components of the reactor encompass facilities such as thermal insulators, piping, pumps, heat exchangers, heat control sections, fuel processors, control systems, heaters, and power regulators [64].

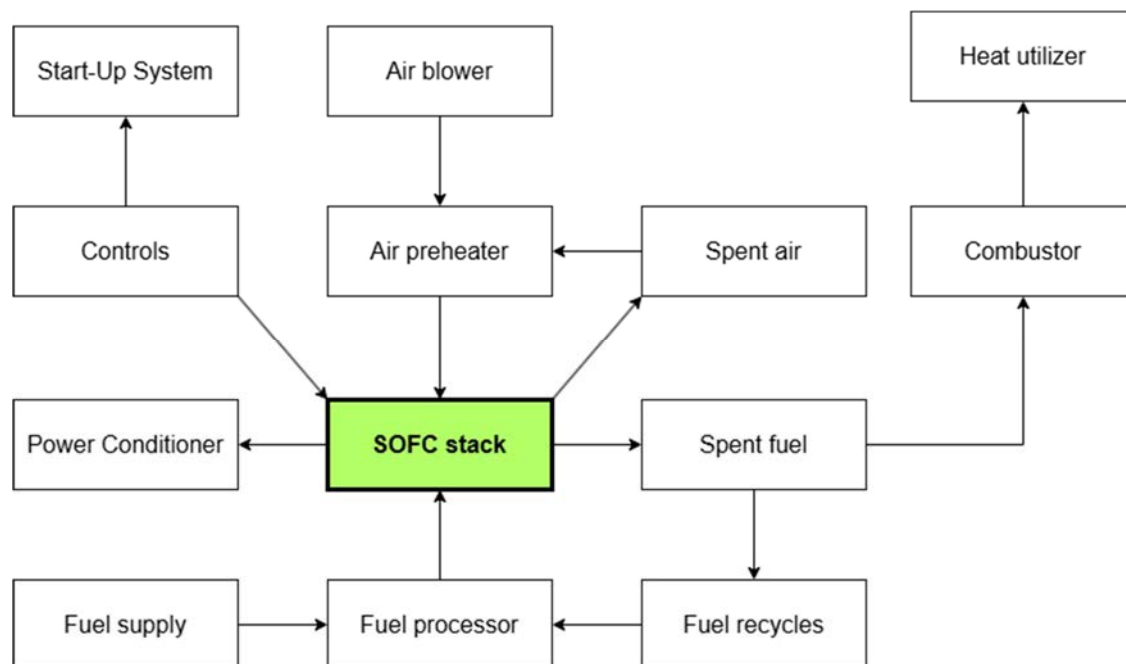


Figure 2. 7 Schematic representation of a SOFC.

Essentially, fuel cells are engineered to serve as alternatives to large-scale power generation units, including power plants, ships, and locomotives. Over the past decade, the potential for solid oxide fuel cells to function as compact, portable power systems has become increasingly evident.

These systems can operate using natural gas, biogas, or propane [61]. The power output for mobile applications can reach up to 100 We, sufficient for communication purposes. Furthermore, this output can be scaled up to 5 kWe for residential applications. In this context, heat output is of lesser significance, as electrical efficiency is not the primary metric of performance. The principal moving components of this system include air blowers and fuel pumps, provided that compressed fuel is not utilized. All other components, except for the valves, are solid, resulting in reduced maintenance costs for the system. In a compact system, reliability stands as a crucial element. It is important to note that the reliability of these systems surpasses that of combustion engines [56].

Advantages VS disadvantages of SOFC

- Usage of different types of fuels
- The heat generated by the battery is utilized again.
- The presence of hydrogen and carbon monoxide in fuels is correlated by effectively eliminating the need for expensive noble metal catalysts.
- The battery's polarization can be considered negligible. As temperature rises, there is an enhancement in the ionic and electronic conductivity of the battery.
- It can generate electricity with significant efficiency and power output.
- Carbon monoxide and sulfur do not act as poisons for the electrodes of solid oxide fuel cells.
- The elevated temperatures necessitate the use of more expensive materials, which come with certain limitations.
- At a temperature of 1000 °C, the free energy generated by this cell is less than that produced at 650 °C by the molten carbonate fuel cell. Consequently, the open circuit potential of the solid oxide fuel cell is approximately 100 mV lower than that of its molten carbonate counterpart.
- There exists a risk of hydrogen and oxygen infiltrating the electrolyte, which can diminish the fuel cell's efficiency.

2.3.9 Hydrogen fuel cell

The hydrogen fuel cell represents a cutting-edge technology employed in electric vehicles, capable of supplying the necessary electric energy for the vehicle's engine or electric motors through the utilization of hydrogen gas. A significant challenge faced by electric automobiles is the depletion of battery charge; therefore, an energy converter is integrated into the vehicle to recharge the batteries, thereby extending the driving range. Alternatively, the establishment of charging stations across various regions of the country is essential, alongside the installation of high-capacity batteries [65]. The implementation of such infrastructure for electric vehicles entails considerable financial investment and extensive development of road facilities. An alternative solution for electric vehicles involves the incorporation of internal combustion engines, leading to the creation of hybrid vehicles or those powered by fuel cells. Hydrogen

serves as the source of electricity required for both the battery and electric motor. While the use of combustion engines in electric technology is more prevalent, the production of hydrogen fuel cell vehicles, known as Fuel Cell Electric Vehicles (FCEVs), has seen limited growth in recent years. Hydrogen fuel cells operate through an electrochemical reaction that generates electricity without combustion, combining hydrogen and oxygen to produce electricity, heat, and water [66] .

The application of these devices extends beyond automobiles, as they can be utilized in any environment where electrical energy is required. These devices are composed of three primary components: the Anode, Cathode, and Electrolyte Membrane. Their operation involves the passage of hydrogen through the anode and oxygen through the cathode. Within the anode, hydrogen molecules are separated into electrons and protons; the protons traverse the porous electrolytic pathway to reach the cathode, which contains oxygen. Meanwhile, the electrons flow into the electrical circuit linked to the anode, enabling the fuel cells to generate electrical energy [67]. The process of generating electrical energy also produces heat at the anode, while at the cathode, protons, electrons, and oxygen combine to form water [68]. It is important to note that a single fuel cell is insufficient to meet the energy demands of an electric vehicle; therefore, multiple cells are arranged in series, often numbering in the hundreds, to collectively generate the necessary electricity. This assembly of fuel cells is referred to as a Fuel Cell Stack, indicating a collection of fuel cells. Consequently, the outputs of hydrogen fuel cells include electricity, water, and heat. Additionally, the absence of rotating and mechanical components in these devices ensures that their operation is entirely silent [66].

Advantages VS disadvantages of hydrogen fuel cells

- These devices operate without any mechanical rotating parts, which ensures that they function silently, producing no audible sound.
- The absence of fossil fuel utilization in these devices, along with their ability to generate products like water and heat, leads to the conclusion that they contribute minimally to environmental pollution and are classified as green technologies.
- An additional advantage of avoiding mechanical components is the decreased likelihood of failures and issues in hydrogen fuel cells, resulting in enhanced reliability.
- The device operates on electrochemical reactions rather than combustion for energy conversion, resulting in high efficiency for fuel cells. Furthermore, this efficiency can be enhanced by utilizing the heat generated by the device through the implementation of heat exchangers [67].
- The most efficient fuel cell operates using hydrogen; however, these cells are also capable of functioning with alternative fuels such as natural gas, biogas, and methanol. These alternatives are more plentiful and accessible, allowing for their use in critical situations where hydrogen may not be available. Consequently, these gases can serve as a viable energy source for batteries.
- Unlike lithium batteries, these systems do not degrade over time and can maintain their

functionality for nearly the entire lifespan of the vehicle.

- The limited presence of hydrogen charging stations in various parts of the globe constitutes a major issue for the adoption and functionality of fuel cell electric vehicles (FCEVs).
- The transportation of hydrogen poses significant risks and can lead to considerable waste. Consequently, it necessitates the utilization of robust and durable tanks, which incur high costs for manufacturers. As a result, the process of transporting hydrogen to fueling stations can be both challenging and perilous.
- To extract hydrogen from water, it is necessary to pass an electric current through it. This electricity is often produced by burning fossil fuels, which makes the use of these fuels in automobiles less than environmentally sustainable [69].

2.3.10 Proton exchange membrane fuel cells (PEMFC)

The proton exchange membrane fuel cell (PEMFC), known as the solid polymer fuel cell, was initially created by General Electric in the United States in 1960 for application in NASA's inaugural manned space vehicle initiative.

In these types of systems-batteries, the electrolyte is composed of an ion-conducting polymer. Porous electrodes are positioned on either side of the electrolyte, effectively integrating the anode, electrolyte, and cathode into a single unit. These membrane electrode assemblies are connected in series and utilize bipolar plates for interconnection, as depicted in next Figure. The polymer contains mobile ions, specifically protons (H^+ ions), which allow for performance that resembles that of acid electrolyte fuel cells [45]. Operating at low temperatures, polymer electrolytes enable this type of fuel cell to initiate quickly. The slim profile of the membrane electrode assembly has greatly reduced the fuel cell's volume. Other notable advantages of this configuration include the absence of corrosive fluids and the flexibility for the battery to operate in any orientation [70].

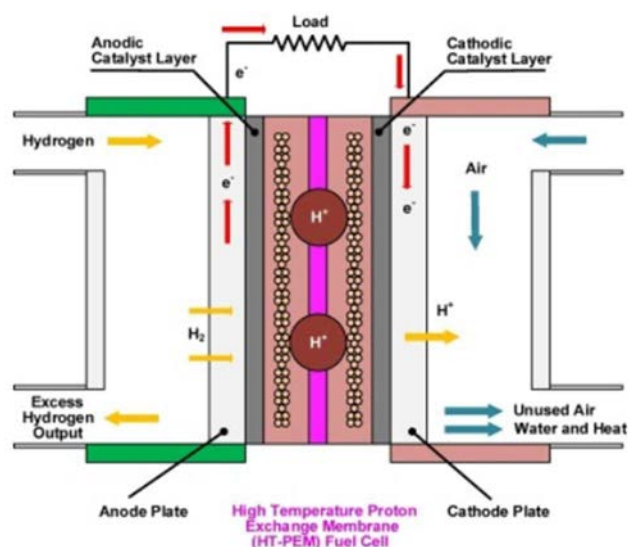


Figure 2. 8 Schematic structure of an HT-PEMFC [46].

The advancements in technology have rendered proton exchange membrane fuel cells particularly advantageous for application in vehicles and various portable devices. Initial prototypes utilized in NASA's Gemini spacecraft were engineered for a lifespan of merely 500 hours, yet they performed admirably within the constraints of their rudimentary missions. Research into this fuel cell technology progressed with the introduction of a novel polymer membrane known as Nafion. This membrane has become the benchmark for proton exchange membrane fuel cells, a standard that remains in use today [71]. Nevertheless, the challenge of effectively managing water within the electrolyte persists, prompting NASA to adopt an alternative technology, specifically the alkaline fuel cell, for the Apollo missions. The General Electric Company ultimately decided to discontinue its commercial pursuits in the development of proton exchange membrane fuel cells. This decision may have stemmed from the higher costs associated with the research and development of this fuel cell technology compared to alternatives, such as phosphoric acid fuel cells. At that time, the catalyst requirement was 28 mg per square centimeter of electrode, a figure that has since been significantly reduced to 0.2 mg per square centimeter or even lower [72].

Progress in PEMFCs experienced a pause during the 1970s and early 1980s. However, interest in this technology was revitalized in the latter part of the 1980s and into the early 1990s, largely due to advancements made by the Ballard Company in Vancouver, Canada, and the Los Alamos National Laboratory in the United States. Recent developments have led to an increase in current density to over 1 amp per square centimeter, while simultaneously reducing the platinum catalyst requirement by a factor of one hundred. The recent modifications and enhancements have led to a substantial decrease in the cost per kilowatt of electricity and have significantly improved power density. PEMFCs are currently undergoing extensive development and refinement for applications in buses, automobiles, and various mobile systems, as well as for combined heat and power solutions [72].

The selection of these fuel cells by NASA for the Space Shuttle Orbiter further underscores their superiority and widespread acceptance. It can be asserted that proton exchange membrane fuel cells have outperformed other electric energy generation technologies due to their adaptability for specific applications. These fuel cells can serve as a power source for a range of devices, from low-wattage applications such as mobile phones and computers to low-kilowatt uses in boats and household appliances, and extending to several tens of kilowatts for vehicles, with capabilities reaching several hundred kilowatts for buses and combined heat and industrial power systems [28].

Nevertheless, various significant elements of fuel cell design exhibit considerable diversity and are influenced by the specific application and the perspective of the designer. The key aspects include the following.

- Water management

- Cooling technique of fuel cells
- The appropriate operation pressure
- The configuration of batteries in a series connection is a significant consideration, as the design of bipolar plates varies widely among different fuel cell types.
- While pure hydrogen is a common fuel choice, alternative reactive substances, such as oxygen, can be utilized in place of air [73].

Platinum is recognized as the most effective catalyst for both the anode and cathode in fuel cells. During the initial investigations into proton exchange membrane fuel cells, a substantial quantity of this metal, specifically 28 mg per cm³, was used. This significant use of platinum contributed considerably to the overall cost of this fuel cell technology. However, in recent years, despite advancements in power output, the consumption of platinum as a catalyst has been reduced to 0.2 mg per cm³. While the fundamental structure of the electrodes remains consistent across various designs of proton exchange membrane fuel cells, the specifics of these designs exhibit considerable diversity. Furthermore, the anode and cathode are often identical, with many proton exchange membrane fuel cells utilizing the same configuration for both electrodes. The platinum catalyst is typically produced in fine particle form and is applied to larger particles of powdered carbon, with XC72 carbon base powder being a common choice for this application. The subsequent process involves one of two available methods, both of which yield similar results. In the separate electrode method, the carbon-based catalyst is affixed to a porous and conductive substrate, such as carbon fibers or carbon paper, often incorporating polytetrafluoroethylene to enhance hydrophobicity and facilitate the expulsion of water generated during the reaction. This addition not only strengthens the mechanical integrity of the electrode but also promotes gas diffusion into the catalyst, leading to the designation of these materials as gas diffusion layers. Each electrode is then secured to one side of the polymer electrolyte membrane [72], [73].

A comprehensive procedure for this process is outlined in numerous articles. Initially, the electrolyte membrane undergoes a cleaning process by boiling in a 3% hydrogen peroxide solution in water for one hour. Subsequently, it is immersed in boiling sulfuric acid for the same duration to ensure thorough protonation of the sulfonate group. Following these treatments, the membrane is rinsed in deionized water while boiling for one hour to eliminate any residual acid. Once these steps are completed, the electrodes are affixed to the membrane, and the entire assembly is subjected to high pressure at a temperature of 140 °C [74]. This results in a fully integrated unit of electrode and membrane. An alternative approach involves fabricating the electrodes directly on the electrolyte. In this technique, a platinum catalyst supported by carbon is applied directly onto the electrolyte, thereby creating the electrode in situ rather than as a separate component. The catalyst, which is frequently combined with the hydrophobic material polytetrafluoroethylene, is applied to the membrane electrolyte through rolling, spraying, or a specialized printing method. The

term "gas spreading layer" can be somewhat misleading, as this component of the electrode serves multiple functions beyond merely dispersing gas. It also facilitates the electrical connection between the carbon-based catalyst and the bipolar plate or any other current-collecting element. Furthermore, the gas diffusion layer aids in repelling product water from the electrolyte's surface and acts as a protective barrier for the delicate catalyst layer. This gas diffusion layer may be integrated into the electrode and membrane assembly or exist as a separate entity [23], [31].

Advantages VS disadvantages of PEMFC

- Remarkable efficiency and power density
- Solid and non-corrosive electrolyte
- Rapid startup
- Operate at low temperatures
- Zero emissions
- Extended lifespan
- Versatility in various applications
- Use of hydrogen or alternative fuels
- Generates usable water
- Sensitive to CO
- High cost of membrane catalyst
- No numerous membrane manufacturers [44]

2.3.11 Microbial fuel cells

Microbial fuel cells (MFCs) promise the generation of renewable energy from organic materials and for the effective treatment of wastewater. To ensure their practical application, careful optimization and precise design are essential. A critical element within MFCs is the membrane separator, which is vital for maintaining the separation between the anode and cathode chambers. Recent studies have highlighted the advantages of membrane-less MFCs in improving power output [40].

However, it is important to acknowledge that such designs may negatively affect the electrocatalytic performance of anode microorganisms due to enhanced substrate and oxygen infiltration, which can result in lower coulombic efficiency. Consequently, when choosing a membrane for MFCs, it is imperative to evaluate factors such as internal resistance, substrate loss, biofouling, and oxygen diffusion. By addressing these aspects diligently, researchers can enhance the performance and efficiency of MFCs, thereby promoting their practical use in sustainable energy generation and wastewater management. Additionally, increased substrate penetration may lead to cathode blockage and bacterial deactivation, further diminishing the efficiency of

microbial fuel cells [40].

The design and optimization of MFCs, particularly regarding the selection and application of membranes, are crucial for their effective use in renewable energy production and wastewater treatment. Additional research is required to address the challenges associated with membrane-less microbial fuel cells and to create enhanced membrane materials for these systems. Next **Figure 2. 9** presents a simplified schematic of microbial fuel cells, demonstrating the process whereby microorganisms are transferred to the anode electrode, enabling electron transfer to the external circuit. Concurrently, protons (H^+) are released and move through the intermediary layer to the cathode, where they react with oxygen from the surrounding environment and an electron from the external circuit, resulting in the formation of water. Thus, the microbial fuel cell functions are based on this fundamental mechanism [34].

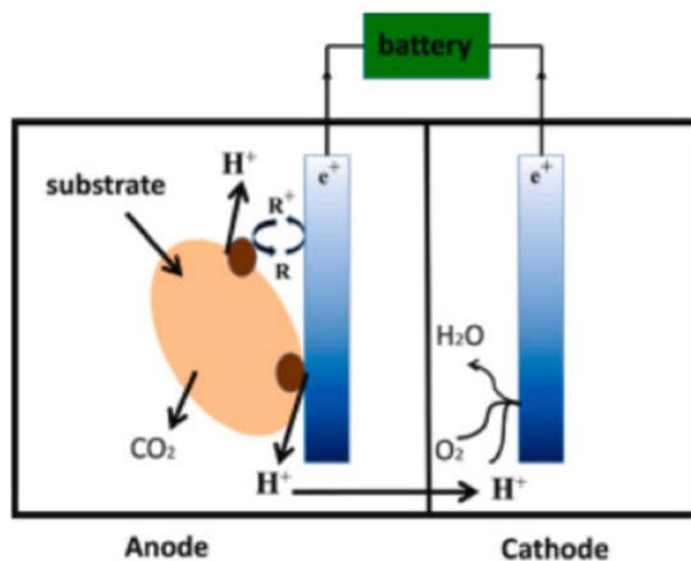


Figure 2. 9 A simplified schematic of microbial fuel cells[49]

2.3.12 Batteries

Batteries are the most extensively adopted means of energy storage, particularly evident in the daily use of mobile phones. The evolution of battery dimensions has been largely shaped by advancements in lithium-ion batteries (LiBs). A significant motivation behind the development of batteries is the imperative for electric vehicles to surpass conventional automobiles, which are powered by fossil fuels. Batteries operation through the cathode, anode, and electrolyte, generate electricity via the chemical reactions occurring within them. The cathode materials typically consist of conductive carbon particles, while metals are generally employed for the anode. Electrolytes can be found in both aqueous and non-aqueous states, with gels also being utilized as electrolytic mediums [75]. Among the various battery types, lithium-ion, sodium-sulfur, lead-acid, and redox flow batteries are particularly prominent. Lead-acid batteries are particularly advantageous due to their high recycling efficiency, with around 99% being collected and recycled in Europe and the United States. They hold the largest market share for rechargeable batteries,

primarily in automotive and industrial sectors. While lead-acid batteries are well-established, cost-effective, and easy to maintain, they necessitate further innovation due to their shorter life cycle, environmental concerns, and lower energy density. In 2016, the World Economic Forum ranked next-generation batteries as the second most significant technological advancement.

Enhancing energy density is a critical objective for these next-generation batteries, achievable through increasing cell voltage, enhancing the specific capacity of anode materials, and reducing the overall weight of the cell. As lithium-ion batteries (LiBs) are regarded as the global benchmark, there is a growing need to explore alternatives due to rising lithium prices and the limitations of energy density. Lithium serves as the anode in these batteries, with common variants including lithium iron phosphate, lithium titanate, and nickel-cobalt-manganese lithium batteries. While these options exhibit high life cycles and stability, lithium titanate is notably more expensive. Nevertheless, it holds significant future potential compared to nickel-cobalt-manganese lithium batteries, primarily due to the high costs and limited availability of cobalt.

Alternatives to lithium include sodium, magnesium, and calcium, with sodium being the most adaptable due to its chemical similarities with lithium-ion battery (LiB) technology. While sodium has been suggested for use with hard carbon as the anode material, it presents challenges such as dendritic growth and a low melting point, rendering it unsafe for anode applications. Magnesium and calcium, on the other hand, have the potential to achieve energy densities that surpass those of LiBs; however, their technological development is hindered by the absence of suitable cathodes and electrolytes that facilitate efficient multivalent ion migration. Additionally, there are other types of rechargeable lithium batteries, including lithium-air and lithium-sulfur (LiS) batteries. Lithium-air batteries utilize a lithium electrode paired with an oxygen electrode, available in both aqueous and non-aqueous forms, and offer greater energy storage capabilities than conventional LiBs. Conversely, lithium-sulfur batteries employ elemental sulfur as the cathode and can achieve energy densities of up to 2600 Wh/kg. However, both battery types face significant barriers to widespread commercialization, such as rapid capacity decline following initial high performance in lithium-air batteries due to oxygen reduction, and problematic interactions between lithium, sulfur, and stabilizing additives in LiS batteries. Furthermore, LiS batteries are prone to safety concerns and operate at lower voltages, while lithium-air batteries struggle with low round-trip efficiency and limited practical air capacity. The emergence of high lithium-conducting ceramic sulfur also paves the way for solid-state lithium batteries, which would be a valuable addition to the market. Given the previously discussed alternatives to lithium, the exploration of sodium-air batteries is a logical progression, and current research aims to address the challenges of dendritic growth and charging stability[41].

Following the trend established by lithium-ion batteries, sodium-sulfur batteries have also been developed and are now commercially operational. Nonetheless, these batteries present safety

concerns due to the flammable properties of sodium and their higher operating temperatures, which range between 300 and 350 degrees Celsius. Flow batteries are a type of rechargeable battery that incorporates external tanks for the storage of electrolytes and electroactive species, which are essential components of the electrochemical cell. The design of the cell influences the power density, while the energy density is contingent upon the size of the tanks. Flow batteries have been utilized in NASA's long-duration space missions and are currently applied in short-term energy storage solutions. Their advantages include affordability, portability, high efficiency, and scalability from kilowatts to megawatts. There are two primary categories of flow batteries: redox flow batteries and hybrid flow batteries. Redox flow batteries consist of two electrolytes separated by a membrane that permits proton transfer, along with two electrodes [32].

During the charging process, the electrolytes circulate through the porous electrodes, and during discharge, the resultant products are directed to the external tank. The vanadium redox flow battery is the most advanced variant in this category. Although it suffers from low power and energy densities, its long-life cycle and durability are notable benefits. Hybrid flow batteries utilize a liquid electrolyte stored externally, with zinc-cerium and zinc-bromine batteries being the most developed types. The latter has been innovated by Exxon and is currently employed by companies such as ZBB Energy, Premium Power, and Redflow Ltd. The integration of microfluidics is a relatively novel approach being explored for flow batteries, aiming to eliminate the need for membranes while achieving high efficiencies of approximately 90% [41].

2.3.13 Supercapacitors

Unlike batteries, which convert electrode materials to generate energy, supercapacitors serve as energy storage systems that utilize two analogous electrodes and store energy through the separation of charges. While they can deliver high power, their energy density is limited to around 5 Wh/kg. The adoption of ionic liquids to replace nonaqueous or flammable electrolytes has emerged as a pivotal area of research. Furthermore, supercapacitors offer benefits when used in conjunction with or as an alternative to batteries, especially considering the limited operational lifespan of batteries [32].

Supercapacitors are categorized into three fundamental types: electrochemical double-layer capacitors (EDLCs), which operate through the adsorption of ions on the electrode surfaces; pseudo capacitors, which function via electrochemical mechanisms involving active materials that participate in rapid faradaic reactions. Pseudo capacitors can be further classified into two distinct types: those that engage in surface faradaic redox reactions and those that facilitate fast ion intercalation at the electrode surfaces. Finally, hybrid capacitors are characterized by their asymmetrical electrodes, which leverage the strengths of both EDLCs and pseudo capacitors. These hybrid devices typically consist of one high-surface-area carbon electrode paired with a

battery electrode, thereby integrating the benefits of energy storage systems, such as supercapacitors and batteries, with lithium titanium oxide proving to be particularly effective in this area [32], [37].

2.3.14 Hydrogen production technologies

The area of hydrogen generation from renewable sources presents a clean and sustainable method for addressing greenhouse gas emissions. Hydrogen boasts one of the highest energy contents among fuels, at 120 MJ/kg, which is significantly greater than that of liquefied natural gas, gasoline, ethanol, methanol, diesel, and propane. Furthermore, hydrogen can be utilized in fuel cells, facilitating the production of clean energy with zero carbon emissions. As a storage medium, it is effective for load-leveling and peak-power shaving, allowing for storage and use as needed. To ensure competitiveness with other hydrocarbons, a production cost of around \$1 per kilogram of hydrogen is considered reasonable. The necessity for hydrogen in powering fuel cell technologies or combustion engines highlights its value as an energy storage medium. Ongoing developments in electrochemical methods for hydrogen production encompass low-temperature water electrolysis, high-temperature water electrolysis, and carbon-assisted hydrogen production. Low-temperature water electrolysis, which occurs below 100 °C using either a polymer or alkaline solution as an electrolyte, allows for rapid start-up and shutdown, making it suitable for integration with intermittent renewable energy sources [76].

Although commercially available, these systems are associated with high costs. Conversely, high-temperature water electrolysis, operating at 700 to 800 °C, involves the electrolysis of steam and is distinct from (SOFC) operations. While the technical feasibility of this technology has been established, the operational costs have hindered its commercialization [77].

The most common techniques of electrolysis encompass alkaline electrolysis, recognized as the earliest method, along with polymer electrolyte membrane electrolysis and solid oxide electrolysis. Current patent activity in hydrogen production indicates that electrolysis ranks as the third most patented technology, accounting for 24% of patents, while photovoltaic electrolysis and photo-electrochemical electrolysis follow with 4% and 1%, respectively. Carbon-assisted electrolysis, despite its lower research intensity due to slow kinetics and the formation of films on active surfaces, proves to be a more efficient method compared to water and steam electrolysis. A recent review has also highlighted membrane reactors as an additional pathway for hydrogen production. While traditional methods for hydrogen generation include fossil fuel reforming and coal gasification, ammonia decomposition utilizing plasma technology has emerged as a highly efficient hydrogen production method. It is important to recognize that various pathways may be more suitable for specific applications. In scenarios demanding zero emissions, high purity of the

final products, and no limitations on operational costs, electrolysis is preferred; however, this preference does not hold when hydrogen is to be derived from organic materials or hydrocarbons [76].

2.3.15 Electrochemical reactors

Electrochemical reactors present a significant advantage by enabling the conversion of energy into various forms, thereby simplifying transport and storage while yielding valuable products. Reactors that facilitate partial oxidation, hydrogenation, and dehydrogenation make use of either oxygen or hydrogen ions, or they incorporate mixed ionic conducting membranes along with electrodes or catalysts on both sides. The movement of species such as O_2 or H^+ occurs under the influence of an applied electric field or differential partial pressure, leading to product formation. The growing trend of 3D printing technologies has streamlined the prototyping process in reactor design, which has contributed to further optimization, enhanced yields, and scale-up studies. Generally, parallel flow reactors are favored for their ease of reproducibility in flow profiles, while microflow reactors are particularly advantageous for optimization studies due to their high conversion rates, reduced IR drops, and the presence of multi-flow channels that facilitate intermediate reactions with various substrates [78].

2.3.16 Other technologies

The alkali metal thermo-electrochemical energy converter (AMTEC) is a less commonly utilized electrochemical conversion device. It harnesses thermal energy from nuclear, combustion, or solar sources to transform thermodynamic energy into chemical energy. This process employs a solid metal electrolyte, typically composed of sodium or potassium beta alumina, along with a liquid metal working fluid. The movement of the liquid metal, driven by heat, results in vaporization, creating a high-pressure environment at the anode and a low-pressure environment at the cathode. This pressure differential generates a voltage signal. Although AMTEC has found applications in space, it faces challenges related to low voltage and power density, necessitating the exploration of alternative design solutions. While certain technologies meet energy consumption needs, as discussed in earlier sections of this paper, an integrated approach combining energy production, storage, and load distribution devices may prove to be the most effective strategy for designing energy management systems [79].

2.4 Water Management

The analysis of the proton exchange membrane indicates that an adequate quantity of water is essential within the polymer electrolyte; otherwise, there will be a reduction in current conductivity. It is essential to ensure that the water content does not reach a level that would obstruct the pores in the electrodes connected to the electrolyte, as this could lead to saturation of

the gas diffusion layer. Therefore, achieving an optimal balance of water is crucial and necessitates meticulous attention. In proton exchange membrane cells, water is generated at the cathode, and ideally, this water maintains adequate moisture levels in the electrolyte. Air circulates over the cathode, providing the necessary oxygen for the battery while also facilitating the evaporation of a significant amount of water. Given the thin nature of the electrolyte, water can easily migrate from the cathode to the anode, ensuring that the entire electrolyte remains properly hydrated without encountering major issues. While this favorable condition is typically achievable, it requires precise engineering design to realize. However, certain challenges arise; notably, during battery operation, H^+ ions migrate from the anode to the cathode, carrying water molecules along with them, a phenomenon often referred to as electroosmotic stretching. It is observed that for each proton, between one and five water molecules are extracted. This phenomenon indicates that, particularly at elevated current densities, the anode side of the electrolyte may experience drying, even when the cathode is adequately wet. Additionally, a significant challenge arises from the drying effect of air at high temperatures. Notably, at temperatures exceeding 60 °C, air tends to evaporate moisture from the electrodes at a rate that surpasses the production of water from the reaction between hydrogen and oxygen. A potential solution to this issue involves humidifying the air, hydrogen, or both prior to their introduction into the battery. While this approach may appear unconventional, as it introduces a by-product that could hinder other processes, it is evident that this practice is sometimes essential and can substantially enhance the battery's efficiency. One of the significant challenges encountered is maintaining an appropriate balance of water within the pile. In practice, certain areas may exhibit optimal conditions, while others may be excessively dry, and some may be inundated with water. A pertinent illustration of this issue is the analysis of the air flow through the pile. Initially, the air may be entirely dry upon entering the battery. However, as it traverses the surface of the electrodes over time, it may reach a state conducive to evaporating excess water. Nevertheless, upon exiting, the air can become oversaturated, rendering it incapable of further evaporation of surplus water. This concern extends beyond mere design challenges, particularly in the context of larger batteries and mass fuel cells.

CHAPTER 3

Electrolysis of water – Hydrogen economy

3.1 Introduction

Electrolysis represents a prominent method for hydrogen production, aligning with the Hydrogen Energy Earthshot initiative aimed at reducing the cost of clean hydrogen by 80%, targeting a price of \$1 per kilogram within the next decade. The hydrogen generated through electrolysis can potentially lead to zero greenhouse gas emissions, contingent upon the electricity source utilized. It is essential to assess the electricity source's cost, efficiency, and the emissions associated with its generation when determining the advantages and economic feasibility of hydrogen production through electrolysis. In numerous areas across the country, the current power grid is not optimally suited to supply the necessary electricity for electrolysis, primarily due to the greenhouse gas emissions and fuel consumption linked to the low efficiency of the electricity generation process. Efforts are underway to utilize renewable energy sources—such as wind, solar, hydro, and geothermal—as well as nuclear energy for hydrogen production via electrolysis. While these methods can achieve nearly zero emissions of greenhouse gases and other pollutants, substantial reductions in production costs are required to compete with established carbon-based methods like natural gas reforming [8].

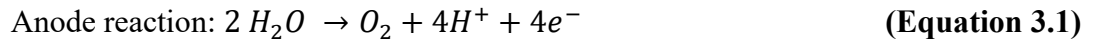
Due to its interfacial characteristics, the electrocatalytic performance is influenced not only by the structure and composition of the electrode material but also by the overall electrode-electrolyte interface, including the properties of the electrolyte in proximity to this interface [80].

3.2 Water Electrolysis

Electrolysis process can be utilized for hydrogen production from water without emitting any carbon dioxide as a by-product. Since there is no carbon dioxide emission in this process, the process is the cleanest hydrogen production process of all the processes if the electricity consumed is produced by RES. Electrolysis is the splitting of water into hydrogen and oxygen through a direct current, i.e., the conversion of electricity into chemical energy. There are around 8 gigawatts (GW) of installed electrolysis capacity worldwide today. Electrolysers can be grouped according to their charge carriers and the electrolyte used, which gives three classes: Solid Oxide (SO) electrolysers, Polymer Electrolyte Membrane (PEM) electrolysers, and Alkaline electrolysers. Similar to fuel cells, electrolysers have an anode and a cathode with an electrolyte between them. Different electrolysis devices operate in different ways, primarily due to the varied properties of the electrolyte materials used [5].

The electrolyte within a polymer electrolyte membrane (PEM) electrolyser is a unique

plastic substance. Water is reacted at the anode to give positively charged hydrogen ions (protons) and oxygen. The electrons move through an external circuit and the hydrogen ions specifically move through the PEM to the cathode. Hydrogen ions combine with electrons at the cathode from the external circuit to give hydrogen gas as shown in Equations 5-6 below.



Alkaline electrolyzers function by transporting hydroxide ions (OH^-) from the cathode to the anode via the electrolyte, resulting in hydrogen production at the cathode. For many years, liquid alkaline solutions of sodium or potassium hydroxide have been commercially utilized as electrolytes in electrolyzers. Recent developments in the use of solid alkaline exchange membranes as electrolytes are demonstrating promising results in laboratory settings [81].

Solid oxide electrolyzers, which employ a solid ceramic electrolyte capable of selectively transporting negatively charged oxygen ions (O^{2-}) at elevated temperatures, generate hydrogen through a distinctive process. At the cathode, water combines with electrons sourced from the external circuit, resulting in the formation of hydrogen gas and negatively charged oxygen ions. These oxygen ions traverse the solid ceramic membrane and react at the anode, yielding oxygen gas and releasing electrons back into the external circuit. It is essential for solid oxide electrolyzers to operate at high temperatures, typically ranging from 700° to 800°C , as this is necessary for the effective functioning of the solid oxide membranes. In contrast, proton exchange membrane (PEM) electrolyzers operate at 70° to 90°C , while commercial alkaline electrolyzers function at 100° to 150°C . The SO electrolyzers can effectively harness the heat generated at these high temperatures, sourced from various means such as nuclear energy, thereby minimizing the overall electrical energy required for hydrogen production from water. The performance metrics of different electrolyser indicates that solid oxide electrolyzers exhibit the highest efficiency, although they remain in the research and development phase [81].

Like fuel cells, electrolyzers are composed of an anode and a cathode, which are divided by an electrolyte. The operational mechanisms of various electrolyzers differ primarily because of the distinct types of electrolyte materials used and the ionic species they facilitate.

Water electrolysis is an electrochemical method that utilizes electrical energy to decompose water into its constituent gases, hydrogen and oxygen [82]. The overall reaction of water electrolysis is expressed as:



In n-type semiconductors, the absorption of photons leads to the generation of electrons and holes when light interacts with the semiconductor. The electrons generated by this process

travel through the external circuit to reach a counter electrode, facilitating the production of hydrogen through the reduction of water. Concurrently, the photogenerated holes migrate to the working electrode, where they contribute to the oxidation of water, resulting in the formation of oxygen. To achieve effective charge separation, it is often necessary to apply an external bias from a power supply, as resistance arises between the two electrodes within the solution at the interface [83]. Consequently, the photoanode and counter electrode engage in two distinct half-reactions.

Water electrolysis is recognized as the initial well-established and commercially effective process to produce pure hydrogen through the splitting of water, a method that was introduced in the late 1920s. This chemical reaction involves the breakdown of water into hydrogen and oxygen using electrical energy. The electrolysis cell serves as a critical component of the electrolytic hydrogen generation system [84]. It is considered the most efficient technique, where the endothermic reaction is propelled by the application of external energy to the electrolyzer, which then electrochemically separates water into hydrogen and oxygen. Data concerning the recycling processes is estimated based on an assumption regarding how much environmental burden can be avoided in total. It is assumed that legislation and resource supply concerns will drive recycling rate (including collection rate) to as much as 80 %, but at the expense of energy efficiency and cost to such an extent that only 50 % of environmental impacts of virgin material production is avoided. The reason for assuming only oxygen gases [80]. This process results in the collection of hydrogen at the cathode and oxygen at the anode, as shown in **Figure 3.1**.

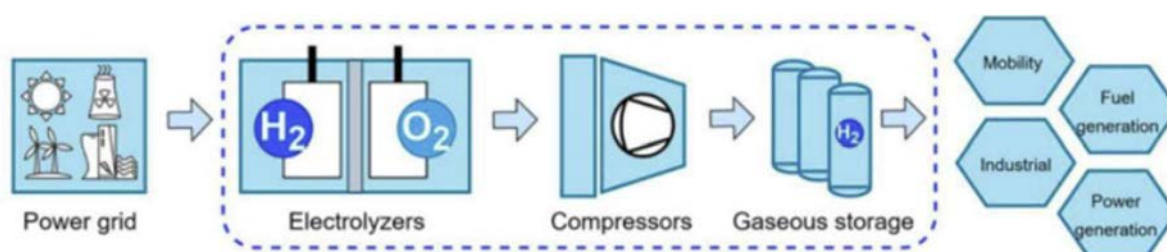


Figure 3. 1. Collection of hydrogen [80].

Three primary technologies can be identified based on the type of electrolyte utilized in the electrolysis cell:

- Alkaline electrolysis, which employs a liquid electrolyte.
- Polymer electrolyte membrane (PEM) electrolysis, utilizing an acidic ionomer electrolyte, commonly referred to as solid polymer electrolysis (SPE);
- High-temperature (HT) steam electrolysis, which incorporates a solid oxide electrolyte.

By the late 1960s, the production of industrial hydrogen shifted towards fossil-based feedstocks, which remains the main source of hydrogen generation today. Currently, electrolysis contributes only about 4% of the total hydrogen produced worldwide. Several literature reviews provide in-depth analyses of hydrogen production methodologies. Other research has also detailed the

technical aspects of various hydrogen generation techniques through electrolysis. A thorough examination of state-of-the-art electrolytic hydrogen production methods was conducted by Ursua et al. Furthermore, numerous other studies have elaborated on hydrogen production techniques, focusing on economic factors, hydrogen storage methods, and their environmental effects and applications [85].

Water electrolysis, in conjunction with proton exchange membrane/polymer electrolyte membrane (PEM), has been developed to enhance the process of electrochemical water splitting. The two main factors that affect this process are efficiency and current density. The energy requirements for an electrolysis unit, both ideal and actual, are defined as the energy needed to drive the reaction. Therefore, the enthalpy H , represented by the equation $H = E + PV$ (where H signifies enthalpy, E represents total internal energy, P indicates pressure, and V denotes volume), for hydrogen production via the water splitting reaction, $H_2O \rightarrow H_2 + 1/2 O_2$, aligns with the enthalpy of water, which is calculated to be $H = 285.813 \text{ kJ/mol}$ based on thermodynamic principles [84].

Alkaline water electrolysis involves a gas-tight diaphragm that separates two electrodes. When water is introduced from the cathode side, a direct current (DC) is applied, resulting in the dissociation of H_2O into H^+ and OH^- ions. Hydrogen gas (H_2) is collected in a separate unit, while the OH^- ions migrate through the aqueous electrolyte to the anode side, where they generate oxygen gas (O_2). The role of the diaphragm is to isolate the two reactions, effectively stopping the mixing of hydrogen and oxygen gases. It is constructed to be permeable to water ions yet impermeable to gases. To boost ionic conductivity during the reaction, a liquid electrolyte, usually a concentrated aqueous solution of potassium hydroxide (KOH), is incorporated. Other electrolytes, such as sodium hydroxide (NaOH) and sodium chloride (NaCl), have also been used. However, a significant limitation of alkaline electrolytes is their tendency to be corrosive [80].

Traditional electrolyzers employ a diaphragm material made of 3 mm thick asbestos, which limits their operational temperature to 80°C . The cathode typically consists of steel that is activated through a coating of various catalysts, while the anode is predominantly constructed from nickel or nickel-coated steel. The separation between the two electrodes is approximately 5 mm. The energy generated by an alkaline water electrolyzer is largely influenced by the characteristics of the electrodes and the operational parameters. Alkaline water electrolysis is recognized as a widely utilized technology, as its electrolyzers can produce hydrogen at both high and atmospheric pressures [80].

High-pressure electrolyzers generate hydrogen at pressures between 6 bar and 30 bar, with the potential to reach up to 200 bar. In contrast, atmospheric pressure electrolyzers operate at pressures not exceeding 6 bars. Furthermore, high-pressure electrolyzers exhibit a specific energy requirement of approximately 4.5 to 5 kWh/Nm^3 of hydrogen, while atmospheric pressure electrolyzers require about 4.1 to 4.5 kWh/Nm^3 . Conversely, high-pressure electrolyzers can achieve an efficiency of up to 78% based on higher heating value (HHV), whereas atmospheric

pressure electrolyzers can attain efficiencies of up to 85% HHV. Research indicates that the lifespan of an alkaline water electrolysis system can extend to 30 years, with diaphragms and electrodes needing replacement approximately 2 to 3 times throughout this period. In summary, alkaline water electrolysis demonstrates promising outcomes and stands as the most widely utilized electrolysis technology in commercial applications. Numerous industries globally employ these systems due to their inherent safety and durability [86].

Recent developments have significantly enhanced the efficiency of electrolyzers, with a primary objective of reducing the operational costs associated with electricity consumption, which correlate closely with the cell surface area of the electrolyzer. Moreover, advancements have been made by replacing diaphragm materials with ion-exchange inorganic membranes. A cutting-edge alkaline water electrolyzer system has been introduced, capable of functioning at temperatures up to 150 °C. This system is designed for large-scale hydrogen gas production, achieving a purity of up to 99.9% without the necessity for purification equipment [87].

The Proton Exchange Membrane (PEM) system, often referred to as the solid polymer system, employs a compact polymer membrane that is notably thin. Nafion, a common material used in this context, typically has a thickness of less than 0.2 mm and operates without the need for a liquid electrolyte. In comparison to alkaline electrolyzers, PEM systems exhibit a reduced operational lifespan. Water is introduced at the anode, where it is dissociated into H^+ ions that migrate through the membrane to the cathode, resulting in the generation of hydrogen gas (H_2) and oxygen (O_2), which remains in the aqueous phase. Noble metals, such as platinum or iridium, are frequently utilized as electrode materials [25]. Unlike alkaline water electrolyzers, PEM electrolyzers are available for commercial use in small-scale hydrogen production. These systems can generate hydrogen at pressures reaching up to 15 bar, with an operating temperature around 80 °C. Furthermore, the hydrogen produced can achieve a purity level of up to 99.9%, with a specific energy requirement of approximately 6–8 kWh/Nm³ H_2 and an efficiency ranging from 67% to 82%. PEM electrolyzers are typically operated using a variable power supply. However, a significant drawback of PEM electrolyzers is the substantial initial investment needed for the membrane and noble metal electrodes, which is essential for enhancing commercial production capabilities [86], [87].

The process of water electrolysis requires a catalyst to facilitate an increased reaction rate and current density. Both homogeneous and heterogeneous catalysts have been utilized for this purpose, with platinum (Pt) frequently serving as a heterogeneous catalyst in the electrolysis reaction. Conversely, homogeneous catalysts are characterized by their affordability and high turnover rates, making them viable options for future exploration. Hydrogen (H_2) is produced through the electrolytic splitting of water; however, the high energy consumption of electrolyzers has resulted in elevated production costs relative to other large-scale technologies. According to

various reports, an alkaline electrolysis system has achieved hydrogen production of approximately 0.38 million kg per year, with an energy requirement of 53.4 kWh/kg H₂ and an efficiency rate of 73% [80].

The initial experiments in water electrolysis were conducted and documented by Jan Rudolph Deiman and Adriaan Paets van Troostwijk in 1789. These experiments utilized electricity generated by an electrostatic machine, which was then discharged onto gold electrodes submerged in water. In 1800, Alessandro Volta introduced his newly invented voltaic pile to the process of water electrolysis, although the outcomes did not garner significant attention. That same year, W. Nicholson and A. Carlisle executed water electrolysis experiments employing copper electrodes, which resulted in oxide formation at the anode, alongside the use of a voltaic pile. Shortly thereafter, J. Ritter achieved what could be termed 'true' water electrolysis, successfully collecting oxygen and hydrogen gases separately [88]. Despite these encouraging early advancements, the industrial utilization of water electrolysis did not commence until the late nineteenth century. By 1902, over 400 electrolysis units utilizing alkaline electrolytes were operational. Various technical and engineering challenges contributed to this prolonged delay, particularly the time needed to develop appropriate direct current (DC) power sources. However, the creation of efficient diaphragms for the separation of anode and cathode chambers likely posed an even greater challenge. Consequently, throughout the twentieth century, most technological advancements were closely tied to research and development focused on diaphragm membrane materials [84].

At present, hydrogen plays a crucial role as a chemical agent in the synthesis of ammonia, methanol, petroleum products, various polymers, and numerous other compounds and materials. The predominant method of hydrogen production in the industrial sector involves steam reforming of fossil hydrocarbons, primarily methane, which contributes to atmospheric pollution. The significant emissions of CO₂ into the atmosphere and their detrimental effects on the environment necessitate the exploration of alternative solutions. To establish a carbon-neutral and environmentally sustainable economy, the implementation of water electrolysis for hydrogen production is deemed essential, alongside the development of solutions for distributed, on-demand, and on-site generation [82].

A variety of water electrolysis technologies exist, applicable at both laboratory and industrial scales, with distinctions primarily arising from the type of electrolyte utilized in the cells. The three predominant categories of commercially available water electrolyzers include alkaline water electrolyzers (AWE), proton exchange membrane cells (PEM), and solid oxide electrolysis cells (SOEC). The first two categories typically function under near ambient temperature (NAT) conditions, generally ranging from ambient temperatures up to 90 °C, while high-temperature SOECs operate at temperatures between 700 and 950 °C. Numerous companies

are currently manufacturing commercial electrolyzers of the alkaline and PEM types in series production [88]. Smaller water electrolysis units, with capacities of less than 10 kW, are employed in applications such as gas chromatography, hydrogen welding, meteorology, and on-demand hydrogen production at the laboratory level. In contrast, larger units find use in sectors such as metallurgy, pharmaceuticals, food and beverage production, glass manufacturing, and electronics. Within the energy sector, electrolytic-grade hydrogen serves as a cooling medium for turbine generators and is also utilized in bubble chambers of nuclear power plants. Emerging applications, particularly in mobility, are becoming increasingly prevalent. The expanding market for electrolytic-grade hydrogen is fueled by the necessity for energy storage from renewable and nuclear sources, enhancements in smart-grid energy flexibility, and the establishment of refueling stations for hydrogen-powered vehicles [87].

The surplus energy generated by nuclear reactors has the potential to facilitate the large-scale production of electrolytic-grade hydrogen, serving as an alternative to hydrocarbon reforming. The concept of 'nuclear-hydrogen power,' which involves utilizing the energy produced by nuclear reactors for extensive hydrogen production from water, began to take shape in the early 1970s. This hydrogen can be applied across various sectors, including industry, power generation, transportation, and domestic applications. For instance, the excess electrical energy produced during off-peak hours by a nuclear power facility can be harnessed for hydrogen production, storage, and subsequent re-electrification through electrochemical combustion in fuel cells as needed [25]. Consequently, a hydrogen cycle or hydrogen battery can be implemented to facilitate load shifting in nuclear power plants, effectively eliminating inefficient operational modes and helping to maintain nuclear generation costs in line with nominal load requirements.

Similarly, hydrogen energy storage may be utilized in renewable energy power plants, as well as within the emerging concept of the 'Internet of Energy.' This concept represents a progressive trend in smart-grid development that merges information technology with energy management. Various terms such as Energy Internet, I-Energy, Internet of Decentralized Energy, Transactive Energy, Energy Cloud, and FREEDM Systems are associated with this idea. Hydrogen serves as a versatile energy carrier, and due to its adaptability, electrolysis can be effectively combined with Power-to-X technologies, where X can represent gas, heat, mobility, and more [25].

Hydrogen can be readily produced via LT electrolysis at almost any scale using only water and electricity as inputs. This process is well-established but requires a high input of electrical energy in order to produce hydrogen. From a thermodynamic perspective at 25 °C, 1 liter of hydrogen requires a minimum 3.55 kWh of electrical energy as an input. This increases to around 4.26 kWh when electrochemical cell losses are considered. If the electrolysis process is carried out at HT, then it is possible to utilize some of the heat to produce hydrogen. This contribution

can be high with up to 1/3 of the energy required to produce the hydrogen coming from thermal energy at around 1000 °C [89], [90]. In next **Figure 3.2**, the thermal energy input under cell operation may be slightly different due to internal heating of the cell resulting from current passage, however, due to the difficulty in making an estimate, it has been assumed to be the same as that under open circuit cell conditions. The HT electrolysis systems use an oxygen ion (O^{2-}) or proton conducting (H^+) ceramic as the electrolyte. The process is the reverse to that of a solid oxide fuel cell (SOFC) with many similar materials used for cell construction [91]. The thermal input required for HT systems can be supplied from different sources including renewable or sustainable energy sources or nuclear energy. Several different systems have been proposed including the co-locating of the electrolyzer with a solar thermal source, nuclear power stations, or supplying heat produced from the burning of low-grade fuels such as coal [38], [92].

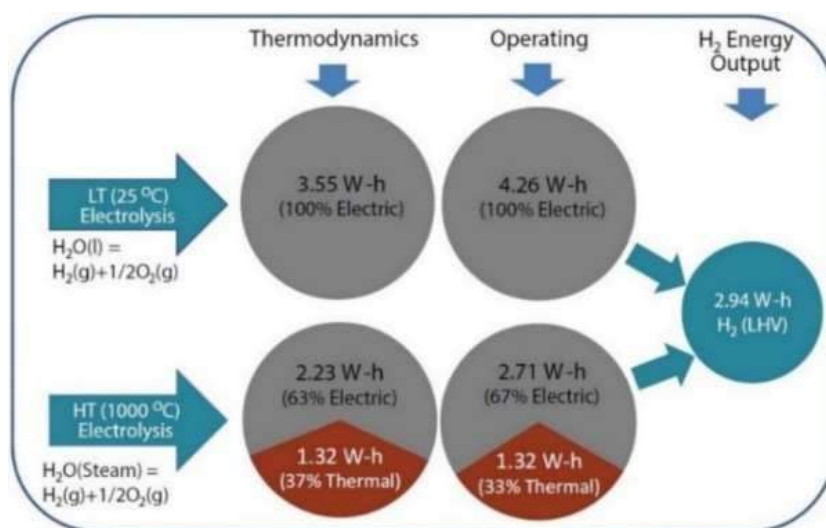


Figure 3.2. The thermal energy input under cell operation[40].

3.3 Short Historical overview

The fundamental equations governing water electrolysis demonstrate that this method can generate clean hydrogen by harnessing electricity from renewable energy sources, thereby avoiding carbon dioxide emissions, unlike the industrial steam reforming of fossil fuels. In recent years, there has been a significant surge of interest in water electrolysis, largely due to advancements in fuel cell (FC) technology across various applications, which has led to an expected increase in the demand for clean hydrogen. Despite being a relatively old technology, with its principles established over 200 years ago, water electrolysis gained initial recognition shortly after Alessandro Volta's invention of the voltaic pile in 1800. In that same year, Anthony Carlisle and William Nicholson in London utilized this device to split water into hydrogen and oxygen, while Johann Wilhelm Ritter conducted similar experiments in Jena, Germany. However, it took many years before the process was applied in practical scenarios [87].

In 1890, Charles Renard developed a water electrolysis apparatus aimed at producing

hydrogen for the French military's airships. However, due to the more economical production of hydrogen through steam reforming, advancements in water electrolysis technology progressed at a gradual pace. By approximately 1900, it was estimated that over 400 industrial electrolyzers were in operation globally. The 1920s and 1930s saw the emergence of various types of alkaline electrolyzers designed for the commercial generation of hydrogen, leveraging low-cost hydroelectric power, primarily for ammonia fertilizer production. Following World War II, the evolution of alkaline electrolyzers continued, and by the 1970s, several companies, including Bamag, Demag, Electrolyzer Corp., Norsk Hydro, Stuart Energy, Oerlikon/Brown, Boveri & Cie, and Lurgi, offered well-engineered systems for industrial use. Nevertheless, for economic reasons, the hydrogen market's share remained relatively small [62].

The advancement of advanced alkaline electrolyzers began in the years following the oil embargo imposed by the Organization of the Petroleum Exporting Countries (OPEC). This crisis highlighted the impending end of the era of inexpensive oil and underscored the necessity for alternative fuel sources. Consequently, research efforts led to enhancements in cell design, the development of superior electrode materials, and the introduction of innovative system concepts for electrolyzers. Concurrently, in the 1970s, General Electric (GE) initiated the development of proton exchange membrane (PEM) electrolyzers. This emerging technology presented various advantages compared to alkaline electrolyzers [84]. However, due to the high cost of materials and a limited operational lifespan, PEM electrolyzers found their place primarily in niche applications and laboratory settings, characterized by low hydrogen and oxygen production capacities.

As stated by the US Department of Energy, electrolysis (EL) represents only around 1.6 million tons of the total global hydrogen output, which stands at 50 million tons each year. The predominant use of hydrogen occurs on-site, primarily for the synthesis of ammonia for fertilizers through the Haber process and for the hydrocracking of heavy petroleum into lighter components [25].

3.4 Polymer electrolyte Membraned Electrolyzers

In a polymer electrolyte membrane (PEM) electrolyzer, the electrolyte consists of a specialized solid plastic material. At the anode, water undergoes a reaction that produces oxygen and positively charged hydrogen ions (protons). The electrons generated in this process travel through an external circuit, while the hydrogen ions migrate selectively across the PEM to reach the cathode. At the cathode, these hydrogen ions react with electrons from the external circuit to generate hydrogen gas.

The anode reaction can be represented as: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ **(Equation 3.4)**

The corresponding cathode reaction is: $4H^+ + 4e^- \rightarrow 2H_2$ **(Equation 3.5)**

3.5 Alkaline Electrolyzers

The operation of alkaline electrolyzers is based on the transport of hydroxide ions (OH^-) through the electrolyte from the cathode to the anode, with hydrogen being produced at the cathode. Commercially available for many years, these electrolyzers employ a liquid alkaline solution of sodium or potassium hydroxide as the electrolyte. Emerging technologies that utilize solid alkaline exchange membranes (AEM) as the electrolyte are currently showing encouraging results in laboratory experiments.

3.6 Solid Oxide Electrolyzers

The operation of solid oxide electrolyzers is characterized by the use of a solid ceramic electrolyte that selectively facilitates the conduction of negatively charged oxygen ions (O^{2-}) at elevated temperatures, leading to hydrogen production through a unique process. At the cathode, steam interacts with electrons from the external circuit, producing hydrogen gas and negatively charged oxygen ions. Subsequently, these oxygen ions migrate through the solid ceramic membrane and react at the anode, generating oxygen gas and supplying electrons back to the external circuit.

Electrolysis of water has emerged as a commercially viable and promising technology for hydrogen production. This process involves the direct splitting of water into hydrogen and oxygen through the application of electricity and specialized electrolysis equipment, contributing approximately 4% to 5% of the global hydrogen output. Considering the ongoing challenges posed by climate change, the utilization of RES, such as wind and solar power, for water electrolysis has gained significant attention. Currently, there are two predominant types of electrolyzers in use: the alkaline electrolysis system, which utilizes potassium hydroxide or sodium hydroxide as an aqueous electrolyte, and the proton exchange membrane (PEM) system, which employs a solid polymer membrane as the electrolyte [73]. The key characteristics of both alkaline and PEM electrolysis systems are summarized in the next **Table 3. 1**.

Table 3. 1 Characteristics of alkaline and PEM electrolysis systems [73].

Technology	Electrolyte	Temperature (K)	Anode reaction	Cathode reaction	Density	Efficiency (%)
Alkaline electrolysis	KOH/NaOH	333–363	$4\text{OH}^- \rightarrow \text{O}_2 + 4\text{H}_2\text{O} + 4\text{e}^-$	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- + \text{H}_2$	0.1–0.4	50–65
PEM electrolysis	Polymer (NaFion)	293–373	$2\text{H}_2\text{O} \rightarrow 2\text{O}_2 + 4\text{H}^+ + 4\text{e}^-$	$4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$	>16	50–75

3.7 General features of water electrolysis cells

An analysis of the thermodynamics associated with the water splitting reaction indicates that this process is nonspontaneous across a wide range of temperatures and pressures relevant to industrial applications. The Gibbs free energy change for the reaction becomes negative only at temperatures reaching a minimum of 2000 K (1 bar), while temperatures exceeding 4000 K are necessary to achieve

a hydrogen yield of merely 50%. The development of reactors capable of facilitating the thermal dissociation of water under such extreme conditions, as well as the creation of devices, such as membranes, for the effective separation of the resultant H_2/O_2 gas mixtures, presents significant challenges that remain unresolved. Consequently, electrochemical reactors are deemed suitable, as they can effectively split water under normal atmospheric conditions.

A water electrolysis cell consists of a galvanic arrangement featuring two metallic electrodes—one serving as the anode and the other as the cathode—positioned opposite each other and separated by a thin layer of ion-conducting material. An external direct current (DC) power source is employed to modify the Fermi level of each electrode, thereby establishing a potential difference between the two energy levels of the redox couples involved in the water dissociation reaction ($\text{H}_2\text{O}/\text{O}_2$ and $\text{H}_2/\text{H}_2\text{O}$). This potential difference is directly related to the change in Gibbs free energy of the reaction, which is essential for initiating the movement of charge carriers, including electrons in the external circuit and ions within the space between the electrodes. During the electrolysis process, the transfer of electrons at each metal/electrolyte interface triggers two distinct redox reactions, the combined effect of which corresponds to the water dissociation reaction. Notably, the electrodes used in water electrolysis are characterized as gas-evolving electrodes. To prevent the spontaneous recombination of gases, a cell separator that allows ion permeability but restricts gas movement is situated in the ionic phase between the electrodes [5].

Water, in either its liquid or vapor form, is introduced into the cell, while mixtures of water/hydrogen and water/oxygen are collected separately at the exhaust. The rate of gas production can be precisely tailored to meet processing requirements by arranging the appropriate number of cells in series. This configuration of cells is referred to as a stack. The stack is an integral component of the balance-of-plant (BoP), which encompasses various auxiliary equipment necessary for the operation of the water electrolysis unit under standard temperature and pressure conditions, ensuring the delivery of gaseous hydrogen and oxygen with the required purity and dryness levels as dictated by subsequent applications [6].

Next **Figure 3. 3** presents a comprehensive overview of a standard PEM process flowsheet, highlighting its essential functions. The electrolysis stack receives input from an AC/DC power conversion system. Following purification, feed water is intermittently pumped into the anodic circuit. Water is circulated through the anodic chambers to facilitate the reaction and dissipate excess heat.

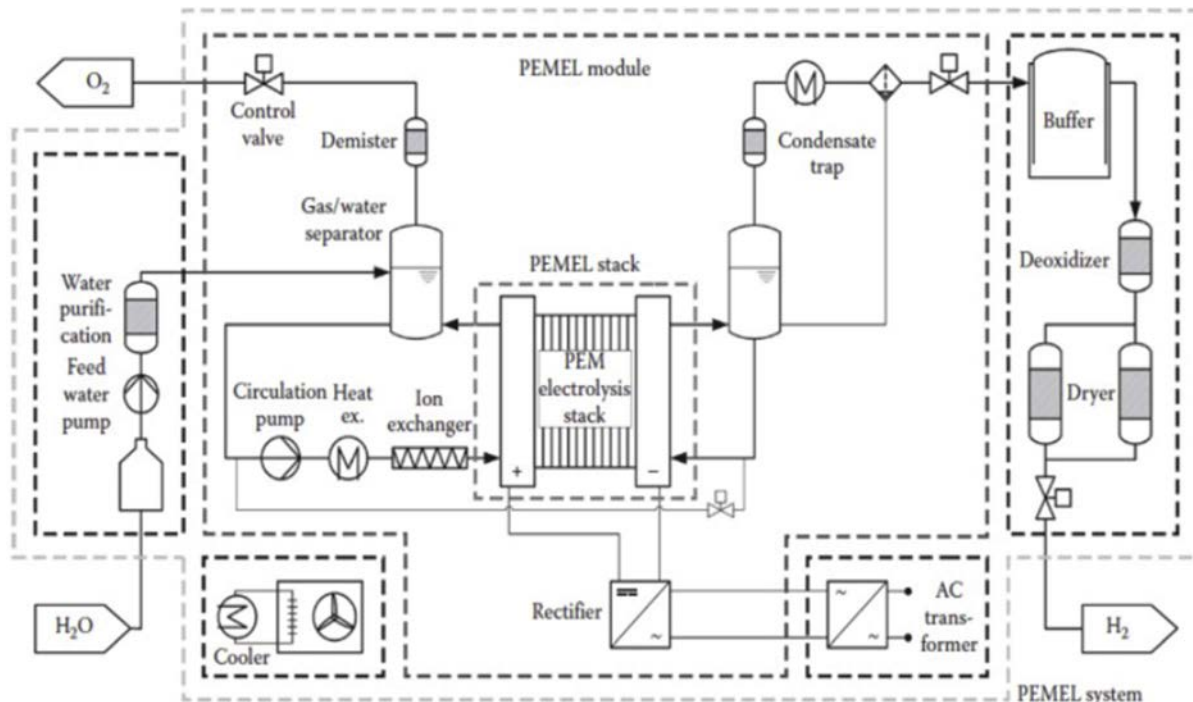


Figure 3. 2 Flow diagram of the PEM water electrolysis process [8].

Water electrolysis is the electrochemical cleavage of water (H_2O) into hydrogen (H_2) and oxygen (O_2).



$$\Delta H_{R0} = +285.9 kJ/mol \quad \text{(Equation 3.7)}$$

Unlike other technologies, water electrolysis does not depend on fossil resources and does not produce greenhouse gas emissions associated with its processes. In fact, water electrolysis does not directly consume any carbon feedstock. As a result, hydrogen produced through water electrolysis is frequently described as carbon-free or "green" hydrogen. However, significant climate change impacts may still occur due to the manufacturing of plants, the development of infrastructure, and the supply chains related to water and electricity.

In comparison to alternative technologies, water electrolysis is unique in that it does not rely on fossil resources and does not emit greenhouse gases during its processes. This method does not involve the direct use of carbon feedstock, leading to the classification of hydrogen produced through water electrolysis as carbon-free or "green" hydrogen. However, it is important to recognize that significant climate change implications may arise from the manufacturing of facilities, the establishment of infrastructure, and the supply chains for water and electricity [62].

3.7.1 Thermodynamic principles

The fundamental component of water electrolysis is the electrolytic cell, which comprises two electrodes and an ion-conducting electrolyte. A direct current is supplied to create a voltage

difference between the electrodes. When a sufficiently high voltage is applied to the electrolysis cell, it triggers an endothermic ($\Delta H_R > 0$) and non-spontaneous ($\Delta G_R > 0$) redox reaction. Depending on the type of electrolyzer used, deionized water undergoes electrochemical decomposition, resulting in the production of either O_2 and positively charged ions (cations) through oxidation or H_2 and negatively charged ions (anions) through reduction at one of the electrodes. The ions then migrate towards the opposite electrode, drawn by its contrasting charge. The electrodes are designated according to the ions they attract; cations move towards the cathode, while anions are directed towards the anode. At the second electrode, the concluding phase of the redox reaction occurs, yielding either H_2 through reduction at the cathode or O_2 through oxidation at the anode [84], [86].

The reaction enthalpy of water splitting (ΔH_R), as shown in previous equation, can be segmented into a thermal segment, characterized by the entropy change (ΔS_R) and the temperature of the process (T), and an electrical segment, represented by the change in Gibbs free energy (ΔG_R). According to the first principle of thermodynamics, the electricity required to electrochemically break down 1 mole of water is equivalent to the corresponding change in Gibbs free energy. Thus, the theoretical voltage (U_{th}) necessary for a water electrolysis cell can be calculated using the number of electrons exchanged per mole of water decomposed ($n = 2$) and the Faraday constant ($F = 96,485 \text{ C/mol}$), which defines the electrical charge per mole of electrons.

$$\Delta H_R = \Delta G_R + \Delta S_R \times T \quad \text{(Equation 3.8)}$$

$$\Delta G_R = U_{th} \times n \times F \quad \text{(Equation 3.9)}$$

At standard conditions of temperature (25°C) and pressure (1 bar), the process of water splitting is associated with specific changes in thermodynamic properties: $\Delta G_{R0} = 237.21 \text{ kJ/mol}$, $\Delta S_{R0} = 0.1631 \text{ kJ/(mol}\cdot\text{K)}$, and $\Delta H_{R0} = 285.84 \text{ kJ/mol}$. When all necessary heat for the process is supplied externally, the minimum reversible cell voltage required for water splitting is determined to be 1.23 V. However, in practice, both electrical and thermal energy, which together constitute the total reaction enthalpy ΔH_{R0} , are typically provided in the form of electricity, leading to a thermo-neutral cell voltage of 1.48 V. It is important to highlight that the actual cell voltage (U_{cell}) tends to be significantly higher due to cell overpotential, which arises from activation losses at the electrodes, limitations in mass transport, and ohmic resistances. As indicated in equation 8, this situation ultimately reduces the voltage efficiency of the electrolysis cell (η_V), defined as the ratio of actual to theoretical cell voltage [93].

$$\eta \times V = U_{th} / U_{cell} \quad \text{(Equation 3.10)}$$

The calculation of voltage efficiency is contingent upon the aggregate state of water supplied, utilizing either the lower heating value (LHV) or the higher heating value (HHV). When

liquid water is utilized, the HHV is applied. In contrast, for electrolyzers that operate with steam, efficiency is determined using the LHV, as the energy required for water evaporation has already been provided prior to its introduction into the electrolyzer. Additionally, it is important to clarify whether the generated hydrogen (H₂) is intended for energetic use (LHV) or chemical applications (HHV), and whether the oxygen by-product will be further exploited. Another method for assessing the efficiency of an electrolyzer involves calculating the ratio of the energy content of the produced H₂, based on its HHV (3.54 kWh/Nm³) or LHV (3.00 kWh/Nm³), to the specific electricity consumption required to generate 1 Nm³ of H₂ under standard conditions (W_{el}). By factoring in the energy requirements of the entire process equipment, one can derive the efficiency of the overall hydrogen production system.

$$\eta \times LHV = LHV / W_{el} \quad \text{(Equation 3.11)}$$

$$\eta \times hHV = HHV / W_{el} \quad \text{(Equation 3.12)}$$

3.8 Electrolysis technologies

The three leading technologies for hydrogen production via electrolysis are alkaline water electrolysis (AEL), polymer electrolyte membrane water electrolysis (PEMEL), and high-temperature solid oxide water electrolysis (SOEL). The differences among these technologies are primarily based on (1) their developmental stage, (2) the electrolyte and charge carrier used, (3) the standard operating conditions, and (4) their capability to operate dynamically in response to variable power supply from renewable energy systems [25].

Each electrolysis technology presents its own set of advantages and disadvantages. Among these, Alkaline Electrolysis (AEL) stands out as the most advanced and commercially viable option currently available. The Proton Exchange Membrane Electrolysis (PEMEL) has exceptional capability to operate dynamically in alignment with the fluctuating availability of electricity produced from intermittent renewable energy sources. Notable features of PEMEL include its ability to achieve high current densities, a compact system design, safe operation at high pressures without the need for subsequent compression, energy-efficient standby modes, rapid response times, and a wide operational range while ensuring high purity of the produced gas. For a comprehensive comparison of the three electrolysis technologies, including their key parameters and the primary technological advantages and disadvantages, please refer to the relevant literature [94].

3.8.1 Process description

A typical PEMEL cell includes (1) a solid polymer electrolyte, (2) two electrodes, namely the anode and cathode, which are equipped with precious metal catalysts, (3) two porous transport layers, and (4) two bipolar plates, as is shown in next **Figure 3.4** [28], [93].

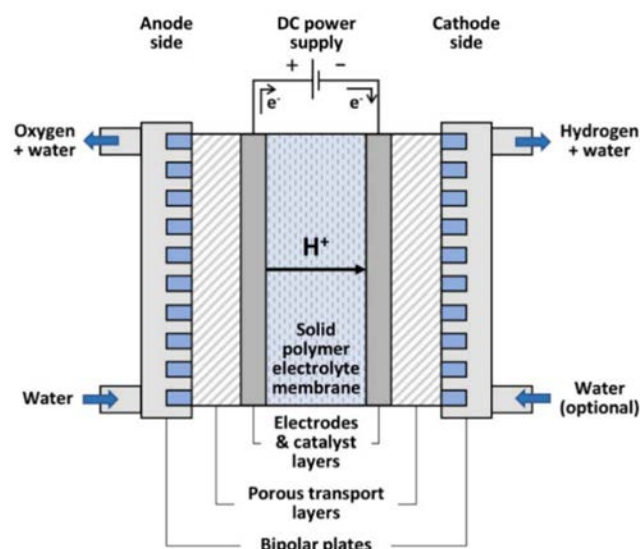


Figure 3. 3 Schematic of PEMEL cell[28].

3.9 Hydrogen economy

The global call for the transition to alternative energy sources arises because fossil fuels harm the climate and create continuing ecological challenges. Seasonal variations and geographical limitations often create imbalances in the availability of renewable energy from these sources. To ensure a reliable energy supply in extensive electricity networks, it is crucial to integrate an energy storage system that can manage the fluctuations in renewable energy output and provide additional energy during peak demand. Although there are various established energy storage technologies, including flywheels, batteries, capacitors, and compressed air, their limited energy storage capacity underscores the necessity for a more advanced high-capacity energy storage solution to effectively harness renewable energy. Hydrogen storage is one such solution that is currently under investigation by many scholars and researchers. This system offers large-scale and long-term energy storage capabilities, which can significantly contribute to decarbonization initiatives and advance the renewable energy sector, thanks to the appealing energy capacity and environmentally sustainable properties of hydrogen [94].

Hydrogen has the potential to be employed across various industries, including transportation, heating and cooling, energy production, and the manufacturing of fertilizers, methanol, and ammonia. This versatility is projected to generate a substantial global market demand of \$276.6 billion by 2032. With a remarkable specific energy capacity of 120 MJ/kg, hydrogen is also recognized for its clean combustion, yielding only water as a byproduct when utilized in fuel cells. However, despite its high energy content per mass, hydrogen exhibits a relatively low volumetric energy density, measuring 0.01 MJ/L at ambient conditions and 8.5 MJ/L when liquefied. In contrast, gasoline and methane offer volumetric energy contents of 32 MJ/L and 0.04 MJ/L, respectively. Consequently, large-scale hydrogen storage is essential to support the economic viability of the hydrogen supply chain. While surface hydrogen storage

systems are currently available, underground hydrogen storage (UHS) is gaining significant interest from major industries. This method is considered safer, less prone to fire hazards, and more cost-effective than surface tanks, with ample underground storage options found in salt caverns, saline aquifers, and depleted oil and gas reservoirs. The International Energy Agency (IEA) has identified UHS as the most practical solution for large-scale and long-term hydrogen storage.

Underground hydrogen storage (UHS) projects can advance rapidly by leveraging understandings gained from underground gas storage (UGS) and carbon dioxide catch and storage (CCS) initiatives although they are relatively recent developments. The principles that guide the selection of UGS sites and the composition and frequency of injection and withdrawal cycles are important for UHS projects and multiple storage techniques also play an important role in these projects. Nevertheless, it is essential to consider the physiochemical distinctions between hydrogen and other gases typically stored, as highlighted in next table. Hydrogen molecules possess a lower molecular mass and density compared to methane and carbon dioxide, resulting in a significantly higher permeability of gaseous hydrogen, which diffuses at a rate several times greater than that of methane in solid matrices. This characteristic necessitates careful geological site selection, emphasizing the importance of low permeability caprocks to mitigate leakage risks. Furthermore, the solubility of hydrogen in water at normal temperature and pressure (0.00016 g/100 g) is markedly lower than that of methane (0.0023 g/100 g) and carbon dioxide (0.169 g/100 g), thereby minimizing the potential for hydrogen loss through dissolution in brine during UHS operations. Additionally, it is crucial to maintain hydrogen losses due to diffusion within the range of 0.1% to 1% during UHS [88], [93].

Table 3. 2 Physiochemical properties of hydrogen, carbon dioxide, and methane [87].

Properties	Hydrogen	Methan	Carbon dioxide
Molecular mass (g/mol)	2.016	16.043	44.009
Gas constant (J/kg K)	4124.2	518.28	188.92
Density at NTP (kg/m ³)	0.08375	0.6682	1.842
Specific gravity (air = 1)	0.07	0.55	1.52
Critical temperature (°C)	−239.96	−82.59	31.06
Net heating value (MJ/kg)	120–141.7	50–55.5	–
Dynamic viscosity at 20 °C (10 ^{−5} Pa s)	0.88	1.1	1.47
Critical pressure (bar)	13.13	45.99	73.83
Critical density (kg/m ³)	31.43	162.7	468.19
Solubility in water (g/100 g) at NTP	0.00016	0.0023	0.169

The data presented in previous **Table 3.2** indicates that the significantly smaller size of H₂ compared to other gases raises important safety considerations during underground hydrogen storage (UHS). It is imperative to thoroughly assess the integrity of geological storage sites and to closely monitor the gas storage process. The effects of gas mixtures with varying concentrations of H₂, as well as the changes in storage locations during the cyclic phases of hydrogen injection

and withdrawal, necessitate comprehensive monitoring to ensure the safety of UHS operations. Furthermore, the success of a UHS initiative is contingent upon various operational factors, which include, but are not limited to, geological characteristics such as geo-storage pressure, temperature, salinity, and rock wettability, as well as geochemical interactions between fluids and rock or minerals, and potential microbial-induced organic contaminations. The abiotic and geochemical interactions between H_2 and the minerals of the host rock warrant thorough investigation, as certain minerals may adversely affect the process by leading to hydrogen loss or jeopardizing the integrity of the caprock. The interaction of injected aqueous hydrogen with formation brine can instigate redox and precipitation/dissolution reactions, resulting in alterations to the in-situ properties of the caprock. Variations in caprock petrophysical properties, including porosity, permeability, wettability, and the propagation or reactivation of micro-fractures, can influence geochemical properties, thereby impacting the long-term viability of UHS. A meticulous geological analysis that considers the implications of in-situ geochemical reactions on hydrogen loss, along with other geological and engineering criteria, is essential prior to the selection of geological sites for hydrogen storage [87].

The loss of hydrogen during underground hydrogen storage (UHS) can be linked to microbial-induced reactions that thrive under downhole conditions, specifically at temperatures below 403.15 K and pressures under 350 bar. For instance, the presence of sulfur-containing minerals and carbonates can lead to a reduction in stored hydrogen levels while simultaneously fostering microbiological activities that contribute to the generation of methane and hydrogen sulfide (H_2S). Additionally, sulfate-reducing bacteria create an acidic environment that diminishes permeability and accelerates material corrosion in the vicinity of the wellbore through the process of sulfide precipitation. Nevertheless, a thorough review conducted by Perera indicated that microbial alterations are less frequently studied compared to geochemical changes, primarily due to the inherent complexity of biotic interactions. It is also essential to account for hydrogen loss via diffusion in UHS projects, as buoyant hydrogen exhibits greater diffusivity than other gases. However, the influence of diffusion is predominantly significant during the initial phase of UHS, with overall diffusive losses reported to be less than 2%.

The capacity for sealing and the integrity of the caprock are critical factors in reducing storage losses. Ideal gas storage formations often feature anticline highs and up-dip pinch-outs within impermeable layers, frequently accompanied by compartmentalized structures, particularly in proximity to sealing faults. These geological formations play a vital role in preventing gas channeling and caprock fracturing, thereby reducing the risk of hydrogen loss. Additionally, various factors that influence rock-fluid interactions during underground hydrogen storage (UHS) include alterations in interfacial tension, adsorption, wettability, and solubility. The low wettability of hydrogen in reservoir rocks can lead to its entrapment by nitrogen or similar gases

during the extraction and recovery phases. The loss of hydrogen through absorption and desorption is a significant concern, particularly when dealing with larger surface areas. Moreover, the in-situ conditions of the reservoir, including pressure and temperature, as well as the type of cementation material, can greatly influence the absorption and desorption characteristics of hydrogen. In the context of the entire supply chain, the points of hydrogen injection and withdrawal are recognized as major potential leakage sites within the hydrogen storage system. It is essential that the materials employed in borehole installations, along with pipes, gaskets, packers, and other equipment utilized during underground hydrogen storage operations, are compatible with hydrogen and resistant to the geochemical and microbiological reactions. Additionally, this equipment must be designed to withstand hydrogen diffusion and prevent embrittlement.

In contrast to the substantial research dedicated to identifying the opportunities and challenges associated with CO₂ geosequestration, investigations into underground hydrogen storage (UHS) remain notably scarce. Furthermore, there is a dearth of studies that provide an overview of the current state of hydrogen project infrastructure, as well as the global objectives and incentives designed to foster hydrogen development. This information is crucial for assessing global readiness for the adoption of a hydrogen economy. Additionally, there is an absence of a comprehensive overview regarding the losses associated with underground hydrogen storage, which would integrate findings from recent research.

Next **Table 3.3** represents a comparative evaluation of the common hydrogen production technologies.

Table 3. 3. Comparative evaluation of the common hydrogen production technologies [94].

Parameters Considered	Grey H ₂	Blue H ₂	Turquoise H ₂	Green H ₂	White H ₂
Associated color					
Primary production technology	Steam methane reforming	Steam methane reforming with carbon capture operation	Methane pyrolysis	Polymer electrolyte membrane water electrolysis	Drilling
Primary feedstock	Natural gas	Natural gas	Natural gas	Renewable energy and biogas	None. This is a naturally occurring form.
CO ₂ emission	High	Low	CO ₂ -free	Carbon-free	Carbon-free
Technology readiness level (TRL) ^a	Commercial (TRL 9)	Industrial scale (TRL 8-9)	Research & Development (TRL 3-4)	Commercial (TRL 9)	Pilot scale (TRL 5-7)
Process energy requirement (MJ/mol H ₂)	0.27	0.31-0.33	0.48-0.57	0.34-0.39	0.02 ^c
Cost of Production (\$/kg H ₂) ^b	0.67-2.22	0.99-3.18	2.8-4.5	2.24-8.69	<1

In recent times, there has been an increasing focus on using an alternative source of hydrogen known as naturally occurring geologic hydrogen, or white hydrogen. Molecular hydrogen (H₂) is found naturally within the Earth's crust and has been observed to emerge from surface seeps globally. Various geological processes have been proposed to explain the accumulation of hydrogen gas underground, particularly the reactions between water and iron-rich minerals (serpentinization) and the radiolysis of water caused by radiation.

Generally, hydrogen is increasingly becoming a focal point for nations aiming to cultivate green industries, primarily due to its capacity to serve as a medium for the storage and transportation of energy derived from low-carbon or fossil fuel sources. More than 40 countries have established hydrogen roadmaps, which outline strategies for hydrogen supply, domestic production, imports, exports, and applications across various sectors, including steel and chemical manufacturing. According to these strategies and currently announced initiatives, the International Energy Agency (IEA) anticipates that low-emission hydrogen production could reach 38 million tons by 2030. This projection is notable when compared to the existing demand, which is already 2.5 times higher at 95 million tons in 2022 and is expected to escalate to 150 million tons by 2030. Although the demand, supply, and trade of hydrogen and its derivatives are anticipated to expand in the forthcoming decades, numerous questions remain regarding the evolution of the emerging global hydrogen economy, the distribution of environmental and economic benefits and costs, and the equity of this distribution on a global scale. This perspective aims to offer guidance for research to model the future hydrogen economy and to inform policy decisions [94].

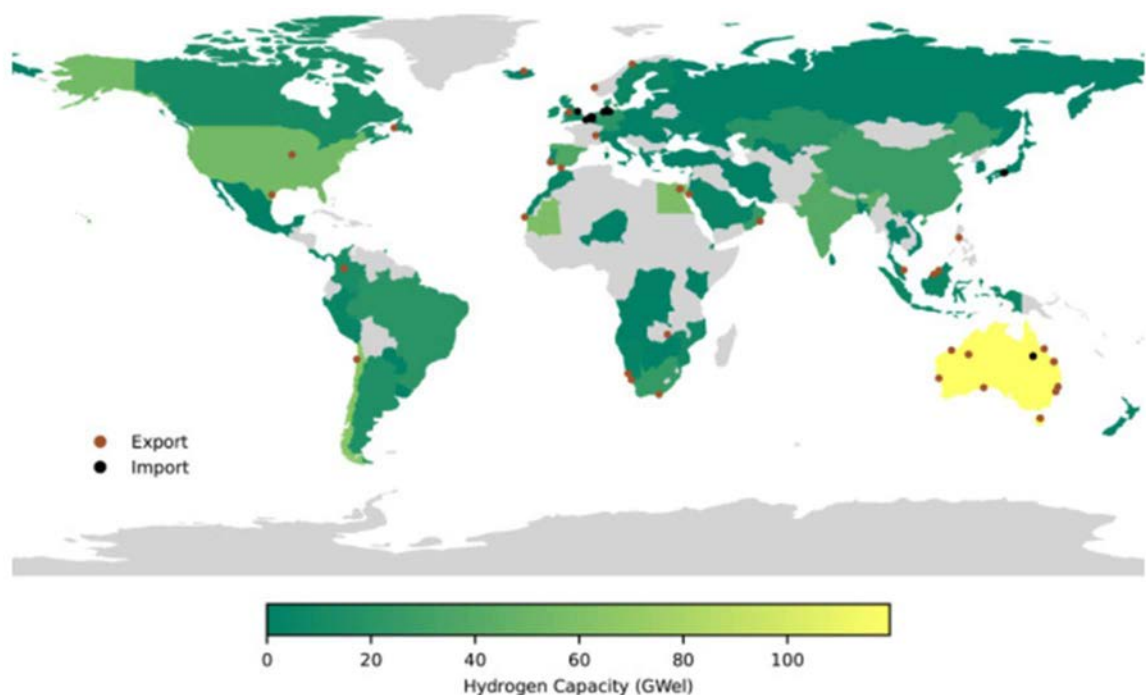


Figure 3. 4 *Planned hydrogen production projects and import/export facilities through 2043. Source: International Energy Agency*

The generation of clean hydrogen does not necessarily ensure its local utilization, which

may result in disparities between regions that could gain economically and environmentally from the industrial activities associated with the hydrogen economy. Nations poised to excel in hydrogen utilization are typically those with established industries in critical sectors; however, these nations frequently lack the resources to produce hydrogen independently, necessitating international trade. As a result, the prevailing framework regarding low-carbon hydrogen has predominantly concentrated on resource-abundant low- and middle-income countries (LMICs) producing hydrogen for export to developed, high-income nations. This situation could yield environmental advantages for high-income countries, as hydrogen may assist in achieving net-zero targets in industries characterized by high emissions. Nevertheless, while affluent nations might implement policy measures to finance projects and development initiatives in exporting countries, they are increasingly adopting a domestic-first strategy concerning associated economic benefits, thereby obscuring the local economic advantages for low- and middle-income producer nations [94].

The discourse surrounding hydrogen is gaining prominence among academics and policymakers regarding transitions to low-carbon energy. A significant portion of the existing literature concentrates on the energy sources utilized to produce low-carbon hydrogen and their classification as clean. Additionally, research explores various facets of the hydrogen economy, including (a) the production technologies available, their costs, efficiency, potential development trajectories, and long-term supply; (b) obstacles to establishing both domestic and international markets, such as technical challenges related to transportation and storage, engagement in global technology exchanges, and disparities in access to low-carbon financing and technology; and (c) the geopolitical ramifications of scaling up hydrogen, particularly how trade and investment in hydrogen will foster new interdependencies and modify bilateral relations among nations.

Recent studies have increasingly examined the beneficiaries and detractors of hydrogen development, along with its implications for global equity. These investigations indicate that the efficiency of clean hydrogen production via electrolysis is on the rise, accompanied by a decrease in costs. This trend presents significant opportunities for low- and middle-income countries (LMICs) endowed with ample water and renewable resources to integrate hydrogen production into their development agendas. Nevertheless, these nations face several obstacles, including limited access to financing, technology, and affordable hydrogen transportation, as well as fluctuations in both domestic and international demand. Such challenges may be particularly daunting for the development of the hydrogen value chain in remote regions that lack established pipeline infrastructures, given the substantial costs associated with building necessary support systems. This research underscores the necessity of incorporating both local and global equity considerations in the establishment of the hydrogen supply chain, particularly regarding the impacts of hydrogen production on water and land utilization, overall energy accessibility, and

emissions in the countries of production.

While the issues of equity within the global hydrogen economy are increasingly recognized, there remains a scarcity of thorough quantitative analyses employing systems models to explore these concerns. Adopting a systems perspective is vital for grasping the comprehensive economic and environmental effects associated with the development of a new global hydrogen value chain, especially considering the regional variations in production and utilization capacities. Effective modeling should draw upon data and insights that reflect the regional dynamics of hydrogen supply and demand, as well as their projected evolution in response to policy changes and market forces. There have been numerous appeals to improve the detailed representation of innovation, infrastructure, policies, and equity in systems models, with notable progress in related areas such as fossil fuels, carbon dioxide removal, and renewable energy. However, these approaches have yet to be thoroughly implemented in the context of hydrogen. Given the international character of this innovative value chain, new modeling efforts can reveal the regional equity implications of expanding the hydrogen economy and pinpoint where policy interventions on the supply or demand side could most effectively enhance equity and facilitate emissions reductions [81], [82].

3.9.1 Altering the conversation regarding the domestic utilization of hydrogen and its derivatives in comparison to exportation

The global hydrogen economy is undergoing significant transformation, marked by a swift increase in the number of nations developing hydrogen roadmaps in recent years. As of September 2021, only 12 countries, accounting for 4% of global emissions from industrial processes, manufacturing, and construction, as well as 7% of global transportation emissions, had established hydrogen roadmaps. However, this figure surged to 45 countries by March 2024, representing 37% of global emissions from industrial activities and 32% from transportation in 2021. To analyze the evolving narrative surrounding hydrogen, we identified the countries with established roadmaps through various sources, including the IEA Global Hydrogen Review for 2022 and 2023, along with the National Hydrogen Strategies and Roadmap Tracker from the Center on Global Energy Policy. We categorized these nations as having an “export focus,” “domestic focus,” or “domestic and export focus,” based on the goals outlined in their national hydrogen roadmaps. Additionally, we enriched our dataset with information regarding the locations of end-use markets and pertinent value chains. This comprehensive analysis highlighted four prevalent characteristics, which we will discuss in detail [95].

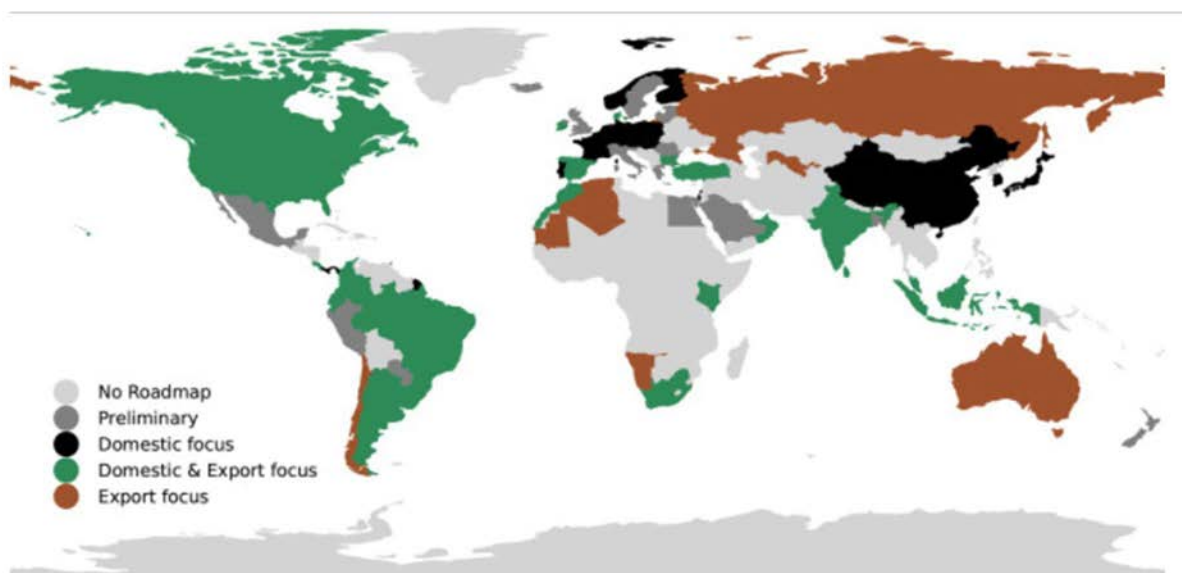


Figure 3. 5 As of April 2024, the status of national hydrogen roadmaps is outlined. In instances where a roadmap is publicly accessible, the color coding indicates whether the roadmap emphasizes domestic hydrogen production and utilization, production intended for export, or a combination of both. In 2021, nations prioritizing domestic hydrogen initiatives and those with dual focuses on domestic and export production contributed to 25% and 11% of global emissions from industrial processes, manufacturing, and construction, as well as 12% and 19% of emissions from the transportation sector, respectively. Conversely, countries concentrating solely on export production accounted for 1% of global emissions in both areas.[87]

3.9.2 Producers of hydrogen who already have established markets are focusing on immediate domestic applications.

Nations that are significant producers of hydrogen are increasingly prioritizing the enhancement of domestic consumption within established end-use sectors, viewing exports as a long-term objective. For instance, Uruguay plans to initiate small-scale hydrogen initiatives aimed at heavy-duty transportation and fertilizer manufacturing in the near term (2022–2025), alongside the establishment of at least two large-scale fuel and fertilizer facilities utilizing hydrogen for export purposes. Following 2030, Uruguay anticipates a rise in domestic demand for fertilizers and transportation. Kenya's hydrogen strategy for the period 2028–2032 includes the goal of substituting 50% of imported nitrogen fertilizer with locally produced alternatives, while potential export avenues for green hydrogen products are earmarked for post-2032. Likewise, Colombia's strategic framework outlines specific goals for the domestic application of hydrogen in transportation and industry by 2030, with plans to export hydrogen to other nations in subsequent years [87].

3.9.3 Hydrogen importers are establishing more ambitious goals for utilization within the domestic market.

Countries that are primarily focused on importing hydrogen, such as Japan, South Korea, and Germany, are revising their strategic plans to incorporate more ambitious objectives. For instance, Japan established a goal in 2017 to achieve hydrogen consumption of 3 million tons annually by 2030 and 20 million tons by 2050, while also aiming for hydrogen to constitute 1% of both the primary energy mix and the electricity supply mix by 2030. In 2023, Japan introduced an

additional target to substitute 1% of the fossil gas in current networks with synthetic methane, produced through the methanation process involving hydrogen and CO₂, by 2030, with an increase to 90% by 2050. Likewise, South Korea initially set a hydrogen demand target of 5.26 million tons per year by 2040 but announced further targets in 2023. Under its revised objectives, South Korea now seeks to achieve 2.1% of total electricity production from hydrogen and ammonia, synthesized from hydrogen and nitrogen, by 2030, and 7.1% by 2036. Germany has also enhanced its electrolyzer capacity ambitions, increasing its initial plan from 5 GW to 10 GW by 2030 [81], [96].

3.9.4 Producers of hydrogen who do not have current markets are emphasizing short-term export initiatives.

Nations that generate hydrogen without established use cases or industries may find it difficult to develop domestic markets in the short term. The primary focus of these nations' announcements and commitments is on hydrogen production for export within this decade. For instance, all hydrogen initiatives in Egypt that were contracted by December 2023 are aimed at exporting green ammonia and methanol during their initial phases, with plans for domestic hydrogen utilization in the fertilizer, steel, and chemical industries anticipated post-2030. Likewise, Namibia intends to initially concentrate on exporting green hydrogen, with the goal of fostering domestic demand over time by capitalizing on the anticipated advantages of the hydrogen sector, such as improved energy access and job creation. However, due to the complexities associated with hydrogen transportation and storage, the volume of exports may be more constrained than expected, particularly for maritime trade. A recent analysis indicated that international hydrogen trade is likely to be confined to regions linked by pipelines, at least in the early stages. Furthermore, this method of delivery encounters its own challenges, as hydrogen requires more energy for compression than natural gas, and dedicated hydrogen pipelines are more expensive than those designed for natural gas [96].

3.9.5 All nations are working to evaluate the parameters that characterize low-carbon hydrogen

There is a growing emphasis on various "colors" of hydrogen beyond just green hydrogen across numerous nations, underscoring the significance of hydrogen as an energy carrier and expanding the definition of low-carbon hydrogen. For instance, the United States intends to enhance hydrogen production utilizing renewable energy, nuclear power, and fossil fuels, along with waste materials through carbon capture and storage (CCS) during the initial phase of its roadmap (2022–2025). Similarly, Brazil is focused on generating low-emission hydrogen from a diverse array of energy sources and feedstocks, including renewables, biomass, fossil fuels with CCS, nuclear energy, waste, and other hybrid methods. Countries like Oman are also aiming to boost hydrogen production and utilization from renewable sources and fossil fuels with CCS, while continuing to produce hydrogen from fossil fuels without CCS until 2050. Furthermore,

there is a variation in the specificity regarding hydrogen sources in the roadmaps of importing nations. Notably, 53% of countries categorized as having a "domestic focus" indicate that the hydrogen they import should be green, whereas 47% are open to importing blue hydrogen or hydrogen derived from alternative sources [52].

These results emphasize the critical need for sustained discussions regarding the suitable role of hydrogen within climate policy, particularly focusing on the intricacies of low-carbon hydrogen, which involves both its production source and its application. From the supply perspective, it is imperative to adopt robust accounting practices to accurately determine the emissions impacts associated with hydrogen produced from clean electricity, with particular attention to electricity generated from dedicated renewable resources or the hourly matching of renewable energy certificates (RECs). For clean hydrogen to effectively lower overall emissions, it must be additional and not replace low-carbon electricity utilized in other sectors. On the demand side, it is essential to focus on applications with limited alternatives for emission reduction, thereby reducing the likelihood of hydrogen production becoming a contributor to increased emissions. This includes sectors that are challenging or impossible to electrify directly, such as heavy-duty transportation, the chemical sector, steel manufacturing, and other industrial processes requiring high-temperature heat, rather than applications in buildings or passenger vehicles where other alternatives are more competitive [81].

Several challenges impede the realization of a clean hydrogen economy, including elevated production costs, the lack of a well-defined value chain, and the necessity for international standards. The significant expenses associated with low-carbon hydrogen production—primarily stemming from the costs of renewable electricity, electrolysis equipment, production inefficiencies, and the intricacies of the steam reforming process—diminish its competitiveness relative to other hydrogen types, such as gray or brown hydrogen. Furthermore, the decarbonization of existing hydrogen usage may lead to increased expenses for carbon capture, utilization, and storage (CCUS) systems, as well as the fuel needed for their operation, in addition to ongoing costs related to CO₂ storage and transportation. The absence of established value chains further obstructs the widespread adoption of green hydrogen and its utilization across diverse sectors. Addressing these issues will necessitate an increase in production capacity, the development of cost-efficient transportation and storage solutions, the creation of new markets, and the promotion of international cooperation. Finally, the lack of international standards hampers the establishment of competitive markets, which are essential for stimulating demand and enhancing value chains [81].

3.9.6 Climate strategies designed to ensure equitable advancement of the hydrogen chain

The swift evolution in the strategies adopted by nations for the production, utilization, and

trade of hydrogen, coupled with the variations in local capabilities and value chains, prompts inquiries regarding the equitable distribution of the advantages and challenges associated with the global hydrogen economy. Furthermore, it raises the question of how to rectify any identified disparities through policy measures. In response to these inquiries, policymakers are increasingly turning to systems models, particularly integrated assessment models (IAMs). Although these models are often technologically sophisticated and encompass a variety of globally traded commodities, such as natural gas and steel, they frequently do not adequately represent international hydrogen trade, with some even omitting hydrogen from the energy mix altogether. Nevertheless, recent advancements have been made in creating a more comprehensive model structure that accurately reflects hydrogen production, distribution, and demand. Additionally, representations of hydrogen-based energy trade have started to be integrated into mitigation scenarios. However, further progress is necessary within the modeling community to enhance this area [97].

The development and scaling of the hydrogen economy in the future is fraught with uncertainty. If it adopts an export-centric model, hydrogen could rival other commodities traded on a global and regional scale, such as oil and natural gas, supported by worldwide value chains. On the other hand, if more nations focus on cultivating local value chains, the emphasis may shift to specialized components or services that can be developed based on local skills and resources, as well as the complexity of the products involved. Understanding both the specific hydrogen developments within individual countries and the expected trade dynamics of hydrogen and related products is necessary for effectively navigating the potential evolution of the global hydrogen economy and creating policies that promote global equity, economic improvement, and climate change mitigation. The policies targeted at promoting equity in each scenario may vary because local value chains may benefit by initiatives such as capacity building and technology transfer and export-oriented sectors may be necessitated by support for equitable emissions accounting and trade reform.

Research into the global advancement of the hydrogen economy is pivotal to the objectives outlined in the Paris Agreement, which highlights the necessity of addressing various equity challenges through financial support, technological innovation, and capacity building. This involves high-income nations facilitating technological development and transferring to low- and middle-income countries (LMICs). Examples of this collaboration include: (a) governments or multilateral banks from high-income countries making direct investments in LMICs, (b) international corporations licensing technologies, making direct purchases, or engaging in foreign direct investment (FDI) and joint ventures within LMICs, (c) institutions providing support or funding for capacity-building initiatives in LMICs, (d) LMICs increasing their domestic investment in research and development (R&D) and enhancing their national capabilities to adopt new technologies, (e) LMICs participating in international cooperative efforts and consortia for research, development,

and demonstration (RD&D) as well as through the United Nations Framework Convention on Climate Change (UNFCCC), and (f) trade mechanisms that promote equitable globalization of production and innovation. The effectiveness of these strategies varies based on the maturity of the technologies and the specific characteristics of the LMICs, with benefits often concentrated in countries with larger markets or more robust existing capabilities. Additionally, measuring these activities in a global stocktake can be challenging. One potential solution to this issue is to implement strategies that also yield advantages for high-income countries and their enterprises. For instance, Japan has established an ambitious goal of producing 15 GW of electrolyzers by 2030, partly to bolster domestic hydrogen production and support Japanese manufacturers of electrolyzers, while also aiming to export some of these electrolyzers to nations lacking adequate manufacturing capacity, thereby enhancing foreign hydrogen production and securing import sources [62], [93].

The exploration of equity in hydrogen value chains can leverage advancements in broader modeling techniques, as well as qualitative and quantitative findings from recent research focused on equity in climate policy, innovation, and technology transfer. Existing literature has identified a variety of dimensions related to international climate equity, with some being explicitly addressed through mechanisms outlined in the Paris Agreement, while others are less clearly represented in global processes. Current frameworks recognize specific equity elements, such as differentiated responsibilities among nations for emission reductions, financial support from high-income countries to low- and middle-income countries (LMICs), and compensation for loss and damage that disproportionately affects low-income nations. Furthermore, additional equity dimensions may overlap with these specific elements, including the recognition of historical consumption disparities, the connections between climate burdens and colonialism, and the necessity of procedural justice in international decision-making. Understanding the interplay between these diverse equity dimensions and critical decarbonization strategies, such as clean hydrogen, is vital for a thorough assessment of policy implications and trade-offs, ultimately fostering synergistic goals for well-being and effective climate action.

The convergence of research on technology and equity corresponds with the growing demand to prioritize equity in systems modeling for the purpose of informing climate policy. Despite recent advancements in this field, there has yet to be a thorough application of these principles to hydrogen. Initial studies have primarily concentrated on evaluating the distributional aspects of climate policies, such as analyzing various interpretations of "fair shares" in climate change mitigation and assessing the distributional effects of emissions reductions on both climate change and public health. Progress in this domain can lead to the creation of new metrics for assessing distributive equity, emphasizing the need for transparency in normative judgments during metric development. Additionally, it is essential to devise methods that address inequities within

model regions, utilizing techniques like microsimulation, downscaling, and integrating models with detailed data sources. Furthermore, equity-relevant outcomes, particularly those associated with sustainable development, should be incorporated into modeling efforts. These initiatives must not only depict the distribution of potential harms but also the benefits, taking into account diverse perspectives, aspirations, and the capabilities of nations to enhance their capacities. The literature underscores the necessity of promoting procedural and recognition equity in systems models by incorporating the viewpoints of a wide array of stakeholders throughout the modeling process [95].

3.9.7 Strategies for Enhancing Future Hydrogen Analysis

It is recommended four strategic avenues for researchers and policymakers to enhance the incorporation of equity considerations within the hydrogen economy into global climate policy dialogues, drawing upon the existing body of literature concerning innovation, technological advancement, and integrated assessment modeling. Firstly, by integrating perspectives on innovation and development related to international technology transfer and the concept of "catching up" in low- and middle-income countries (LMICs), there exists the potential to create greater opportunities for these nations to engage in the hydrogen value chain, thereby reaping benefits from domestic consumption or exports to the global hydrogen market. Secondly, many integrated assessment models (IAMs) require a more nuanced depiction of hydrogen delivery and trade to effectively assess the opportunities and trade-offs linked to various policy and technical decisions. Thirdly, it is imperative for high-income nations to thoroughly evaluate the equity ramifications of their hydrogen economy development. Lastly, policymakers engaged in international initiatives such as Mission Innovation should contemplate the types of research or technology transfer initiatives that could foster the growth of domestic hydrogen industries in LMICs, irrespective of the potential for exports. Additionally, international policymakers must address the challenges associated with verifying the life cycle emissions of hydrogen in instances where hydrogen trade is established [93], [94].

3.10 Problems with the hydrogen economy

It has brought the role of hydrogen to the forefront in the decarbonization process of many sectors globally. The idea of a hydrogen economy has gained much prominence in recent times. The MENA region is strategically located to become a leading producer and exporter of 'green hydrogen' as it is well-endowed with substantial renewable energy resources that allow energy generation at relatively low costs. A vast number of research studies have focused on the possibility of hydrogen production and transportation, using various methodologies to assess the different factors influencing these estimates. There are distinct opportunities for the generation of renewable energy and hydrogen across the MENA countries. The future growth of the renewable energy sector and the possibility of synthetic fuel industries in the MENA region will depend on the assessment

of investment and business risks in each country, considering domestic energy requirements and the establishment of export capacities for synthetic fuels, especially green hydrogen. The Desertec initiative, launched in 2009, aimed at producing renewable electricity on an industrial scale in North Africa for export to Europe. However, it was thwarted by important technical, economic, political, and institutional barriers as well as unexpected situations and internal shareholder conflicts. The lessons drawn from Desertec point to a need for more holistic planning and evaluation. This research will bring these learnings into application, and provide a comprehensive index aimed to address the opportunities in the development of hydrogen, mainly focused on the MENA region [97]. This focus is later reflected in the more general body of literature. Research studies, reports, and other non-peer reviewed literature evaluate some essential requirements for the successful transition toward an economy based on hydrogen. In many cases, this requires the creation of an index that will enable the ranking of countries, identifying regions with high potential for a hydrogen transition, as well as analyzing the strengths and weaknesses of these regions. The consequences of this are far-reaching, as companies can use such indices to determine the most promising locations for future investments and the sourcing of green hydrogen. The identified indices have shown a variety of risks involved in the production of sustainable hydrogen and investments in this field [87]. However, there is a lack of a standardized enumeration of these risks, and even more so a lack of a commonly accepted method of measurement. Most indices, reports, and evaluations about the risks related to a green hydrogen transition offer minimal or no information regarding the specific methodologies applied. These experiences made by the Desertec initiative clearly show the need to use an integrative approach in planning and assessment methodology. The aim of this research work is to use these experiences in making a more specific framework which centers on the potential for hydrogen development, particularly within the MENA region. Similarly, this can also be found within the literature being developed currently. A large number of research papers, studies, and gray literature review the key factors that characterize a successful transition towards the hydrogen economy. This usually involves the creation of an index meant to score countries according to their ability for the transition into a hydrogen economy accompanied by an assessment of their strengths and weaknesses. These indices have important practical implications, as they enable companies to identify the most attractive locations for future investments in green hydrogen. Moreover, these indices have also located several risks related to the production of sustainable hydrogen and related investments in this sector. To date, there is no standardized list of such risks, nor a commonly accepted methodology for their assessment. Most indices, reports, and risk assessments related to the transition to green hydrogen provide little or no information on the specific methodologies they use [97].



Figure 3. 6 Commonly identified challenges of the Desertec vision that may arise in the development of a hydrogen economy[97] .

CHAPTER 4

Advances in nanomaterials for hydrogen storage

4.1 Introduction

Hydrogen is the simplest atom, consisting of a single proton and one electron. As the lightest and most abundant element, hydrogen plays a pivotal role in numerous chemical processes. In its gaseous form, hydrogen is transparent, odorless and non-toxic. However, on Earth, it is only the 15th most abundant element, with a remarkably low atmospheric concentration of approximately 0.5 parts per million. Amazingly, hydrogen contributes to the formation of an extreme number of chemical compounds, the most prevalent of which is water [25].

Hydrogen is a gas under standard conditions, existing as the diatomic molecule H_2 —often called dihydrogen. Hydrogen transitions to a solid state at temperatures of -260.85°C or lower while its liquid state exists only within a narrow temperature range, extending up to -253.25°C . Above its critical temperature of -240°C and pressure exceeding 1.276 MPa, hydrogen is classified as a supercritical fluid.

Hydrogen exhibits unique properties that distinguish it from both conventional and alternative energy sources. These properties include, among others, low mass density, ease of use, exceptionally high energy yield per unit of mass (about 142 MJ/kg) and economic efficiency combined with low environmental impact. Due to these factors, hydrogen is recognized as a promising alternative to conventional fossil fuels. Its potential applications extend across various energy sectors, particularly in electricity generation and the automotive industry, where its environmentally friendly attributes are highly advantageous [93].

Hydrogen, characterized by its single valence electron, exhibits a high level of reactivity and typically forms the diatomic molecule H_2 . In its natural state on Earth, hydrogen is seldom encountered in its pure form; instead, it is predominantly found within a diverse array of inorganic and organic compounds, with water (H_2O) being the most prevalent. This element readily forms chemical compounds known as hydrides with nearly all other elements. The ability of hydrogen to create long chains and intricate molecules, particularly in conjunction with carbon, is essential for organic life, as seen in hydrocarbons and carbohydrates. Furthermore, hydrogen plays a vital role as an energy carrier in the metabolic processes of plants, animals, and humans, being a component of sugars, fats, proteins, alcohols, and oils [93].

There are several methods for storing hydrogen, including the use of high-pressure tanks

and liquefied hydrogen storage systems. Additionally, hydrogen can be stored in solid-state forms, where it is contained within a solid matrix. In this case, the storage density is often specifically attributed to solid material, which facilitates the evaluation and comparison of different hydrogen storage materials and nanomaterials.

Hydrogen storage represents a critical milestone in the advancement of the energy sector. Although hydrogen has high efficiency as an alternative fuel and it is suitable for extensive use in multiple industries, the production process is not easily accessible. Furthermore, hydrogen-related technologies face significant challenges in terms of storage and transportation. As a result, hydrogen storage has become a key focus in the development of a hydrogen-based economy. Due to its low density, the storage of hydrogen at reasonable energy densities poses a technical and economic challenge [82].

For hydrogen to be effectively utilized as an energy carrier, it must be stored safely for varying durations with an efficiency comparable to that of gasoline. Additionally, the handling process must be straightforward and cost-effective. At standard temperature and pressure, 1 kilogram of hydrogen occupies a volume of 12.15 cubic meters and possesses an energy content of 33.5 kWh. In contrast, gasoline requires only 0.0038 cubic meters to provide the same energy content. Therefore, to enhance the competitiveness of hydrogen as an energy carrier, it is crucial to increase its volumetric density. Consequently, three distinct methods for hydrogen storage have been identified: compressed hydrogen storage, liquid hydrogen storage, and solid-state hydrogen storage [81].

In the first method, a large storage tank is essential, along with the availability of gas under high pressure, which consequently requires a considerable amount of compression energy, given that hydrogen gas occupies a large volume. The second method involves the use of a cryogenic liquid, which requires considerable financial investment. Moreover, this process is consistently subject to various losses, such as the boiling off that takes place during refilling, among other factors [93].

The storage of hydrogen in solid form is considered the safest method, as it involves the combination of hydrogen with materials via physisorption or chemisorption. The solid-state hydrogen storage options through absorption are metal hydrides and complex hydrides.

Hydrogen storage materials are critical to enabling practical distribution of renewable energy on a global scale. The following **Figure 4.1** shows the structural models of such materials. They can store hydrogen efficiently at a density higher than that of gaseous and liquid hydrogen storage systems at ambient temperature. Systems involving hydrogen storage materials are, therefore, being evaluated for various applications, especially regarding the global integration of renewable energy [93].

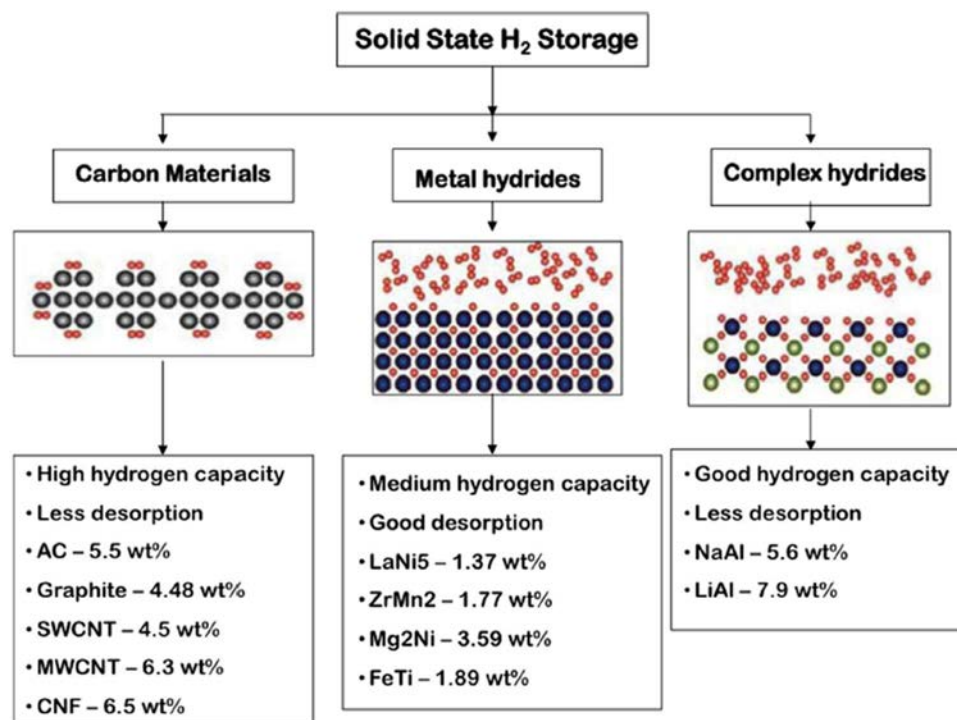


Figure 4. 1 Different solid-state hydrogen storage options [3].

Designing optimized materials and nanomaterials hydrogen storage is a challenging task. Generally, two basic requirements should be considered:

- many adsorption sites per weight and volume of hydrogen storage materials and
- the heat of adsorption of hydrogen storage materials should be increased.

For example, at room temperature, the optimum adsorption enthalpy of hydrogen storage material should be between 10 and 50 kJ and theoretical calculations reveal a value of 15.1 kJ. The combined demands of reversibility of hydrogen loading, high capacity, low volume, low weight, price, safety, and ease of operation mean that currently no material yet meets the constraint for reversible hydrogen storage under near-ambient conditions.

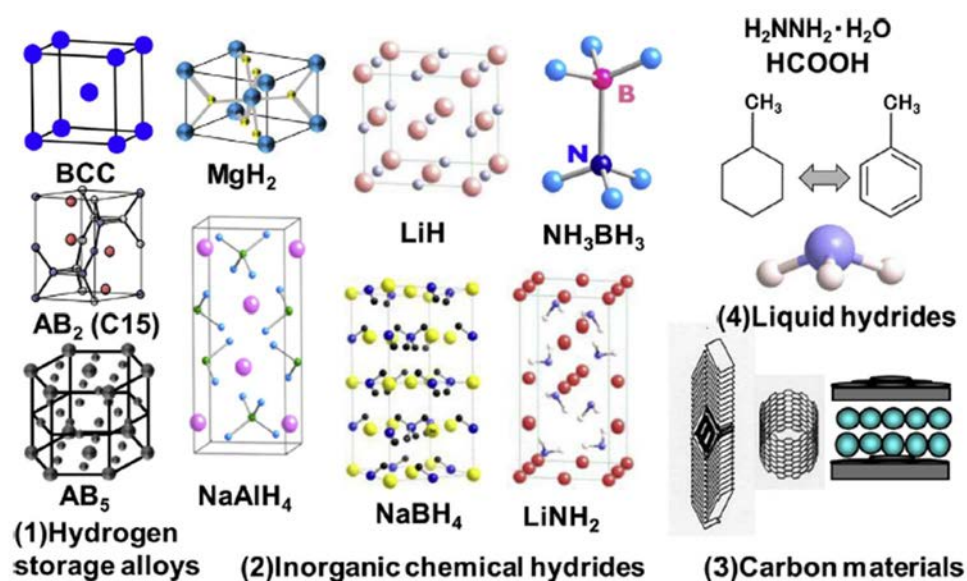


Figure 4. 2 Structural representations of materials used for hydrogen storage [81].

The high demand for hydrogen has been on a consistent upward trajectory in recent years, driven by various factors. In 2022, global hydrogen consumption reached 95 million tons, with a significant portion still utilized in conventional sectors such as the chemical industry and petroleum refining. There is a growing expectation that hydrogen will find applications in emerging fields soon, including biofuel upgrading, electricity storage and generation, integration into carbon-neutral cement production, and hydrogen enrichment in metallurgy. Most regions have seen a substantial increase in hydrogen consumption, apart from Europe, over the past few years. Regarding global hydrogen production, approximately 95 million tons were generated in 2022, primarily sourced from fossil fuels. While the technologies for hydrogen production and its applications are well-established, the safe and efficient storage of produced hydrogen remains an area that requires further exploration. One of the key technological challenges that hinders large-scale hydrogen utilization, such as in hydrogen fuel cell vehicles, is the development of an effective storage system. Furthermore, the demand for hydrogen storage is anticipated to rise in tandem with the growing discrepancies between hydrogen consumption and production, a trend that can be anticipated from the rapid increase in hydrogen manufacturing worldwide [81].

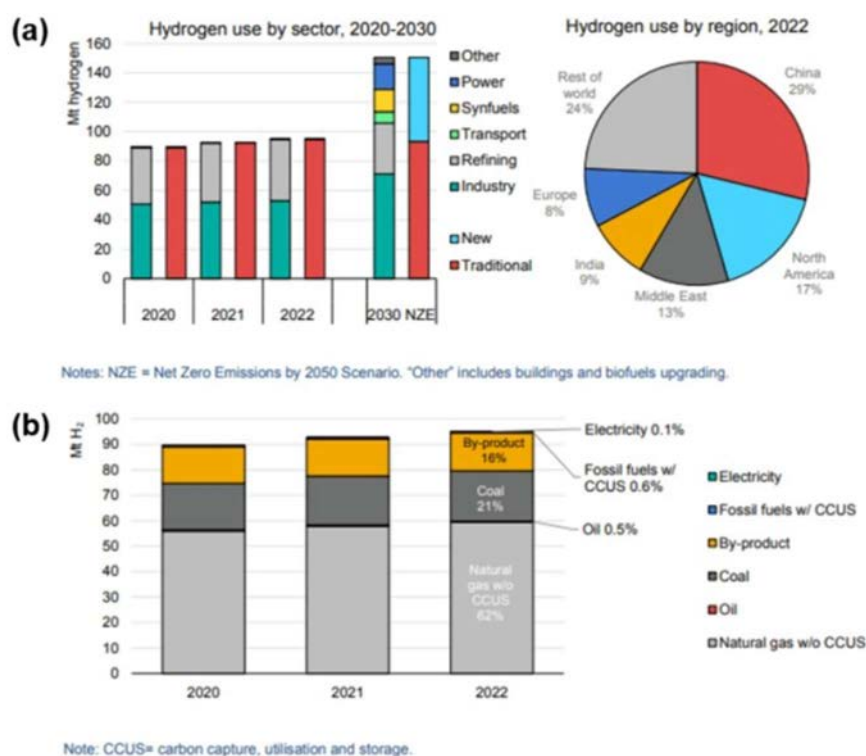


Figure 4. 3 Statistics of hydrogen use by sectors in 2020–2030 and by region in 2022 (a), and hydrogen production via different technologies from 2020 to 2022 (b). Reproduced under the terms of the CC-BY 4.0[87]

4.2 Compressed Hydrogen storage

High-pressure cylinder storage is currently the most widely used method for hydrogen containment. However, the amount of hydrogen that can be stored within practical transport- and stationary-use volume is limited. Although it uses a technique capable of extremely high pressures in a range of 700–800 bar, it is characterized by a relatively low volumetric density; its energy

content cannot be near those associated with gasoline under similar conditions. Moreover, more apprehensions arise with respect to the potential embrittlement of the cylinders themselves. Furthermore, substantial expenses associated with mechanical compression aside from the large drop in pressure encountered in the gas cylinder under hydrogen release, especially refueling a hydrogen fuel cell vehicle, are other facets that need consideration [93].

4.3 Hydrogen Storage in Liquid Phase

The liquid form of hydrogen storage offers a capacity that is double that of high-pressure hydrogen storage. However, the volumetric storage capacity is still insufficient, reaching only half of the levels specified by the Department of Energy (DOE). Furthermore, the high costs involved in the liquefaction process must be addressed, as well as safety issues concerning the handling of cryogenic tanks and the risks of evaporation losses [98].

4.4 Solid State Hydrogen Storage

Hydrogen storage in its solid state, accomplished by means of synthesizing metal hydrides—intermetallic hydrides and complex hydrides—was, until quite recently, an especially auspicious way to store hydrogen in a technically and safety-effective manner. It, indeed, exhibits very large volumetric capacities—beyond the limitations related to pressurized or liquid hydrogen. The mechanism of solid-state storage relies on the unique properties of certain metals that can absorb hydrogen due to their ability to incorporate hydrogen atoms into their metallic lattice structure. Furthermore, the relatively low pressures used in this storage method add to its classification as a safer option. A comparison of these technologies, focusing on volumetric capacity and the associated technological challenges, is shown in the following **Table 4. 1**.

Table 4. 1 A comparative evaluation of the leading hydrogen storage technologies, emphasizing their volumetric capacity and the technological challenges they present.

Storage technology	Volumetric density	Technological challenges
Compressed gas (800 bar)	40	Safety, Cost, Pressure drop during use, Embrittlement
Liquid hydrogen (21 K)	71	Safety, Cost, Thermal Losses
Solid-State storage	80-160	-

4.5 Hydrogen storage

The following **Figure 4. 4** illustrates the pressure-density for hydrogen at six different temperatures. At lower pressure levels (up to 15 bar), there is a nearly linear relationship between pressure and density, represented by a straight line. However, at elevated pressures, the increase in hydrogen density does not follow a linear pattern. At a pressure of 300 bar (30 MPa) and a temperature of 30 °C, the hydrogen density approaches 20 kg/m³. When the pressure is raised to 800 bar (80 MPa), the density can be elevated to approximately 41 kg/m³, and at extreme pressures of 2000 bar, the density

may reach 70 kg/m^3 , although such pressures are not technically practical. In the context of a hydrogen refueling station, the hydrogen pressure is typically limited to a maximum of 700 bars. The high-pressure storage of hydrogen enables a significant reduction in volume, compressing 5 kg into 0.125 m^3 at 700 bars. Various types of hydrogen compressors are available, including reciprocating piston compressors, ionic liquid piston compressors, electrochemical compressors, metal hydrogen compressors, and piston-metal diaphragm compressors.

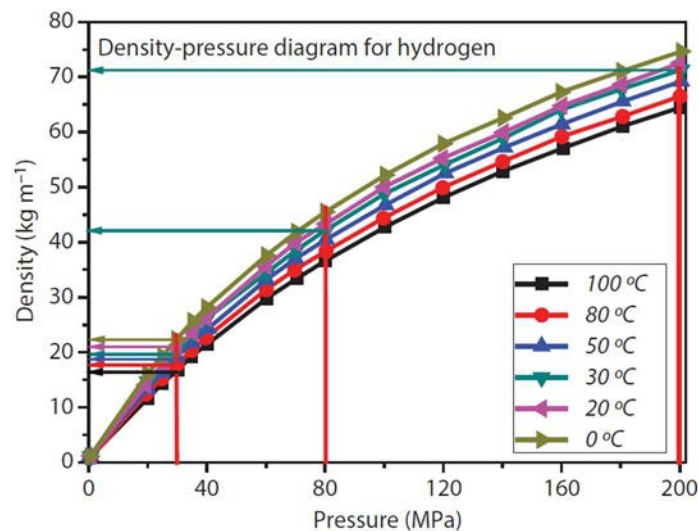


Figure 4. 4 The density of compressed hydrogen as a function of pressure at six temperatures.

4.6 Piston Compressor with Reciprocating Mechanism

The reciprocating piston compressor operates on two fundamental principles: the presence of high-pressure cylinders equipped with small area pistons and hydraulic drive cylinders featuring larger area pistons. Hydrogen compression is facilitated by utilizing hydraulic power to transfer low-pressure hydrogen into the low-pressure hydraulic cylinder, which contains a piston of considerable area. Consequently, the pressurized hydrogen exerts a force on the large piston surface, creating a counterbalancing force against the smaller piston in the high-pressure cylinder. This results in an increase in pressure within the high-pressure cylinder, driven by the disparity in surface areas of the two pistons. The hydraulic piston's movement during its stroke is a critical factor influencing the discharge rate, and the cycle can be self-sustaining by reversing the piston's direction. A significant concern with mechanical compressors is the necessity for the working fluid to be free of moisture to prevent damage or corrosion to the piston surface. Additionally, effective cooling of the hydraulic drive is essential to avoid unwanted temperature increases during compression, thus ensuring high compression efficiency. The compression cycle in a two-stage mechanical compression system is depicted in next **Figure 4. 5** [82].

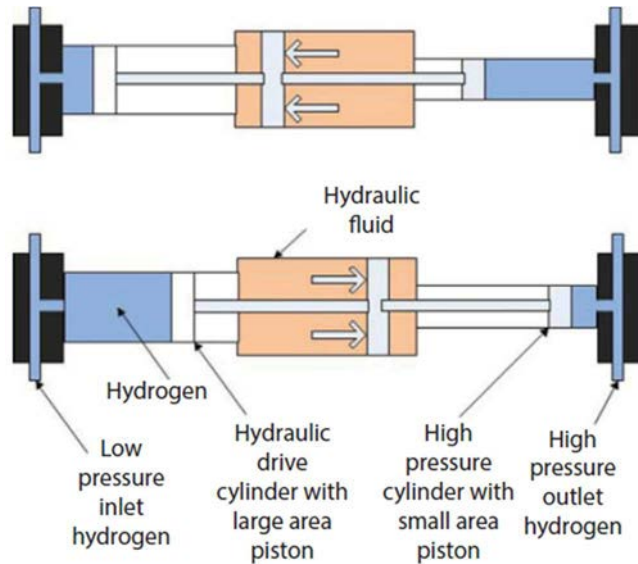


Figure 4. 5 Schematic of a two-stage mechanical compressor [82].

4.7 Ionic Liquid Piston Compressor

The ionic liquid compressor offers a promising alternative to traditional solid piston compressors. This technology offers significant advantages, primarily due to the absence of mechanical moving parts, which mitigates associated operational issues. During the compression process, the liquid effectively extracts heat from the gas, contributing to a reduction in the overall cost of the liquid compressor, attributed to the simplicity of its components and sealing mechanisms. Furthermore, this system is characterized by extended operational longevity and notable enhancements in efficiency. Nevertheless, the specific type of ionic liquid utilized is critical for the compressor's functionality, as certain liquids may decompose under high temperatures. Additionally, the ionic liquid is instrumental in minimizing mechanical losses, thereby further enhancing efficiency. Its properties include low compressibility and minimal gas solubility. A key consideration in the design of these compressors is the careful selection of ionic liquids and construction materials to address potential corrosion challenges, necessitating the use of materials with high corrosion resistance. An illustration of a hydraulic liquid ionic compression system is provided in next **Figure 4. 6**.

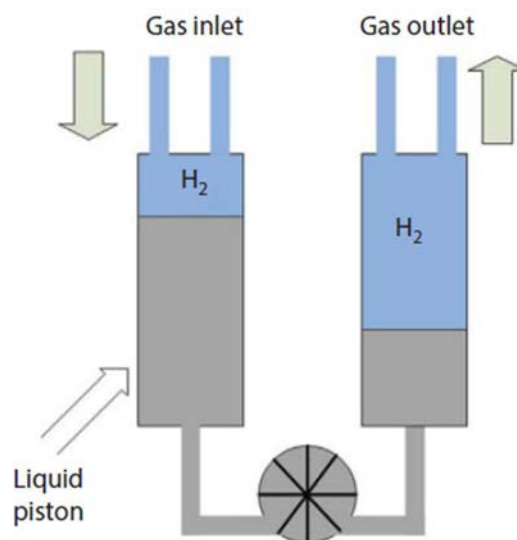


Figure 4. 6 Schematic of hydraulic liquid ionic compressor (LINDE)[82]

4.8 Electrochemical

The operation of an electrochemical compressor is based on an electrochemical cell, consisting of an anode, a membrane electrode assembly (MEA), and a cathode. This compression process is straightforward and does not require any moving parts. Such systems are particularly advantageous when compressing small amounts of hydrogen, as this mode of operation is more efficient. When a voltage is applied, hydrogen undergoes oxidation at the anode, with ions migrating through the membrane to the cathode, where protons are reduced at elevated pressure. To facilitate this process, the cathode compartment must be completely sealed. For achieving higher compression ratios, a cascade configuration, consisting of multiple membrane electrode assemblies, is necessary. The efficiency of electrochemical compression is notable, allowing hydrogen to be compressed from ambient pressure to 16 MPa. Additionally, the power requirements align with isothermal compression, with an expected demand of nearly 10 MW per kilogram for compression to 700 bars. A critical factor influencing the efficiency of the electrochemical compressor is the humidification of the membrane, which must be adequately saturated with water to ensure optimal ionic conductivity. In recent years, various efforts have been made towards the commercialization of this technology, with claims of developing both a single-stage compressor capable of reaching 800 bar and 200 bar, as well as a three-cell stack compressor achieving 170 bars [99].

4.9 Metal Hydride Hydrogen Compressor (MHHC)

The operation of a metal hydrogen compressor can be described in straightforward terms: Initially, hydrogen is stored within the metal hydride at a low supply pressure and temperature. The hydrogen remains contained in the hydride until it is released through an increase in temperature or a decrease in pressure. Subsequently, the stored hydrogen is expelled from the hydride. If the temperature rise is adequate and the final storage volume is less than the supply volume, the hydrogen is released from the metal hydride at pressures ranging from approximately 3 to 10 times the initial supply pressure. A multistage metal hydride hydrogen compression (MHHC) system employs a variety of metal hydrides to enhance the overall compression ratio while optimizing the hydrogenation process at each stage's supply pressure [9].

4.9.1 Operation of a two-stage MHHC

In the two-stage MHHC process, the operation follows a well-defined sequence: Valve 1 opens and the low-pressure electrolyzer is attached to the first-stage reactor. When Valve 1 opens, the first stage absorbs hydrogen in low pressure from the supplier until the hydrogenation process ends. Then Valve 1 closes and the first-stage reactor is in equilibrium. A sensible heating process of the first stage reactor occurs at a predefined high temperature (TH) in order to increase the pressure inside the tank and prepare the system for the upcoming coupling. Valve 2 opens between

the tanks of the first stage and the second stage, where the temperature of the first stage reactor is high (TH) and the temperature of the second stage is low (TL); thus, the released hydrogen from the first stage enters the second stage and is absorbed by the second-stage alloy. At the end of this process, Valve 2 closes. Another sensible heating process takes place at a predefined high temperature (TH) to increase the pressure inside the second-stage reactor. Valve 3 opens, and pressure hydrogen is stored in a high-pressure tank, while reactor 1 is prepared for the next compression cycle [9], [26].

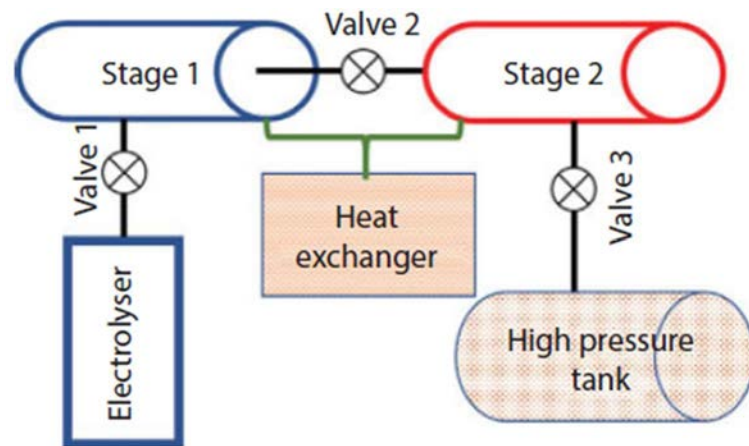


Figure 4. 7 Operation of a two-stage MHHC [57].

The steps outlined above can also be represented by the van't Hoff diagrams pertaining to the first and second-stage materials. The red lines signify the sensible heating process for each reactor, the black dashed line corresponds to the hydrogenation process for both stages, and the black solid line represents the dehydrogenation process. It is imperative that the chosen materials adhere to specific criteria to ensure the safe and efficient functioning of the compression system. The plateau pressure for the hydrogenation process of the first-stage material should be adequately low to facilitate the absorption of hydrogen from the low-pressure hydrogen supplier.

It is essential that the plateau pressure of the dehydrogenation process for the first-stage material exceeds that of the hydrogenation process for the second-stage material. This condition is necessary to maintain a pressure differential between the two reactors, which will serve as the driving force for the transfer of hydrogen from the first tank to the second. Additionally, to attain the maximum compression ratio, the plateau pressure of the final stage should be maximized [87].

4.10 Importance of the Number of stages and Proper Selection

Both two-stage and three-stage compression systems function on the same fundamental principle, which involves the use of metal hydrides arranged in series to compress hydrogen. The primary distinction is based on the number of stages employed, which directly correlates to the variety of materials utilized during the process. In scenarios where stringent temperature and pressure requirements are present, it is advantageous to implement additional stages in the

compression system. For instance, if the heat management system relies on cold and hot water, the operational temperatures during dehydrogenation will range from 90 to 95 °C. Consequently, the compression ratio achievable with a two-stage compressor will be relatively limited, as lower temperatures result in a reduced maximum theoretical pressure compared to the desired target pressure. One potential solution to this engineering challenge is the incorporation of an additional stage or material that is compatible with specific conditions. As previously noted, the careful selection of materials is essential for the efficient functioning of the compressor, ensuring optimal driving force during the inter-stage coupling. Therefore, a three-stage system offers greater flexibility in material selection compared to a two-stage compressor. For example, when analyzing the performance of a three-stage compressor operating between 20 and 130 °C to compress 60 g of hydrogen, a compression ratio of 22:1 was observed. In contrast, a two-stage compression system yielded a similar compression ratio. This comparison highlights the necessity of determining which parameters may need to be compromised to achieve the desired final pressure when choosing between a two-stage or three-stage system, or even a system with more stages. It is important to note that a three-stage system typically results in longer compression cycle durations and increased energy consumption, as additional modules require both thermodynamic and mechanical treatment [31].

Conversely, the ability to increase pressure through an intermediate stage, rather than exclusively via a direct one-step method, allows a three-stage compressor to offer enhanced flexibility and a broader selection of materials. In contrast, a two-stage compression system requires a more rigorous approach to material selection, which may restrict available options. Therefore, it is evident that the choice of an appropriate compression system is influenced by multiple parameters, such as the compression ratio, cycle time, operational conditions, dimensions, and energy consumption [97].

4.11 Nanotechnology

Nanotechnology refers to science and technology dedicated to the precise manipulation of matter's structure at the molecular level. A nanoparticle is identified as a nano-object whose dimensions are within the range of 1 to 100 nanometers, revealing characteristics that are not visible in the bulk material.

The field of nanotechnology refers to the scientific and technological manipulation of materials at the nanoscale. One nanometer is one-millionth of a millimeter, or 10^{-9} meters. For material to be classed as a nanomaterial, it must be smaller than 100 nanometers in at least one dimension. A nano-object is a material that has one, two, or three dimensions within the nanoscale range of 1 to 100 nanometers; by contrast, a nanoparticle is a nano-object in which all three dimensions are within this range. The commonly accepted size limits for nanomaterials, generally

given as either 50 nanometers or 100 nanometers, are justified by the fact that the physical properties of nanoparticles are likely to become like that of bulk materials when their sizes reach these dimensions. Besides, there is an existing definition allowing a top boundary of 1 micron and thus putting the sub-micron range in the category of nano [98], [100].

Nanoparticles can be synthesized primarily through two distinct methods. The conventional method of generating fine particles is known as the "top-down" approach, which involves the reduction of larger materials through attrition and various comminution techniques. In recent years, there has been a growing adoption of "bottom-up" techniques for production. This approach entails constructing a material from the ground up, whether it be atom by atom, molecule by molecule, or cluster by cluster. Both methodologies are crucial in contemporary industry and are likely to remain significant in the field of nanotechnology. Each approach has its own set of advantages and disadvantages. A major drawback of the top-down method is the imperfection of surface structures and considerable crystallographic damage to the processed patterns. Despite the defects associated with the top-down approach, it will continue to play a vital role in the synthesis of nanostructures.

It is crucial to understand that the characteristics of the materials generated can differ markedly depending on the chosen fabrication approach. Besides direct manipulation of atoms, there exist numerous recognized methods for synthesizing nanomaterials, which encompass physical, chemical, and mechanical techniques [100], [101].

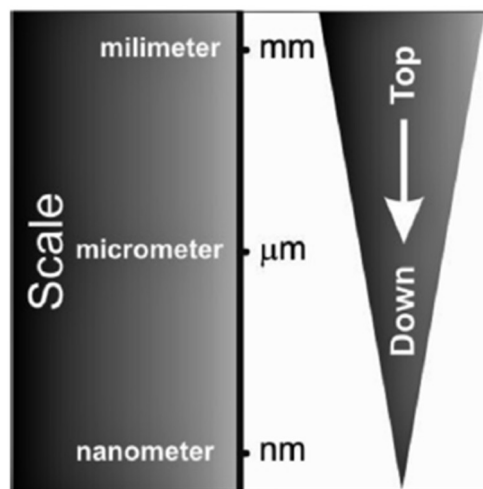


Figure 4. 8 The conventional method of generating fine particles is known as the "top-down" approach [82].

4.12 Methods

4.12.1 Mechanical methods

A variety of methods exist to produce small-grained nanostructures, primarily focusing on the creation of fine-grained powders at the nanometer scale. Mechanical techniques include mechanical grinding, high-energy ball milling, mechanical alloying, and reactive milling. These methods are advantageous due to their simplicity, low-cost equipment requirements, and the ability

to process powders if a coarse feedstock is available. However, challenges such as powder agglomeration and contamination from processing equipment may arise. It is important to note that mechanical processes are typically employed only for inorganic materials and metals/alloys [87].

In high-intensity ball milling, significant impact collisions are employed to transform microcrystalline materials into nanocrystalline structures without altering their chemical composition. A relatively recent technique known as mechanochemical processing (MCP) represents an innovative solid-state method for producing a diverse array of nano powders. This process utilizes dry milling to facilitate chemical reactions through the collisions of balls and powders, leading to the formation of nanoparticles within a salt matrix. The particle size is influenced by the chemistry of the reactant mixture, as well as the milling and heat treatment conditions. The salt matrix helps to minimize particle agglomeration, which can subsequently be eliminated through a straightforward washing procedure [80].

4.12.2 Milling process

The application of mechanical milling for the synthesis of novel alloys, compounds, and nanomaterials was not anticipated until recent decades. Historically, the main purposes of milling have been to mix or blend materials, alter particle shapes, and reduce sizes. Ball milling incorporates both crushing/shearing and impact forces in varying proportions, contingent upon the specific equipment utilized. Numerous types of ball mills have been designed for distinct applications, such as tumbler mills, attrition mills, shaker mills, vibratory mills, and planetary mills, among others. For instance, high-energy milling forces can be achieved using high frequencies and small vibration amplitudes. Given that the kinetic energy of the balls depends on their mass and velocity, denser materials like steel or tungsten carbide are preferred over ceramic balls [102].

The vials utilized in this process are constructed from hardened ferritic steel; however, alternatives such as zirconia, alumina, agate, and hard metal tungsten carbide are also employed to significantly reduce contamination from grinding media, particularly iron. The milling process that produces nanometric structures occurs approximately ten times more rapidly in a SPEX ball mill compared to a planetary ball mill. The duration required to generate fine powders and nanostructures is influenced not only by the material's characteristics but also by various factors, including the weight of the milling balls and the ball-to-powder weight ratio (BPR). This ratio can range from 1 to 100, and typically, the time required to achieve the same powder fineness decreases as the BPR increases. During the milling of pure ductile metals in vials filled with inert gases like argon, phenomena such as agglomeration and cold welding of metal particles to the reactor wall and milling balls, resulting in the formation of balls composed of the milled powder, are frequently observed. Four primary processing methods can be utilized in high-energy ball

milling: (i) mechanical alloying (MA), (ii) high-energy ball milling (HEBM), (iii) mechanochemical activation synthesis (MCAS), and (iv) mechanochemical synthesis (MCS) [101].

4.12.3 Mechanical alloys

The process of mechanical alloying, which emerged in the 1970s at the International Nickel Company, serves as a key mechanical technique for integrating nanosized inclusions into nickel-based alloys. In subsequent years, the mechanical alloying (MA) method has successfully facilitated the preparation of various alloy powders, including those featuring supersaturated solid solutions, quasicrystals, amorphous phases, and nano-intermetallic compounds. This technique has been recognized as a novel and promising strategy for the formation of alloys [23].

The raw materials utilized for mechanical alloying (MA) consist of commercially available high-purity powders with particle sizes ranging from 1 to 100 micrometers. Throughout the mechanical alloying process, the powder particles are intermittently confined between colliding balls, resulting in plastic deformation. This phenomenon is attributed to the generation of numerous dislocations and various lattice defects. Additionally, the collisions of the balls lead to the fracturing and cold welding of the elementary particles, thereby creating clean interfaces at the atomic level. Continued milling results in an increased number of interfaces and a reduction in the size of the elementary component area, transitioning from millimeter to submicrometer dimensions. Alongside this reduction in elementary distribution, several nanocrystalline intermediate phases emerge within the particles or on their surfaces. As the milling duration extends, the fraction of these intermediate compounds increases, ultimately producing a final product whose characteristics depend on the milling conditions [103].

The progression of concurrent mechanical and chemical phenomena can be delineated in the following manner: the application of mechanical stress induces severe plastic deformation, which in turn gives rise to a submicron lamellar microstructure. This is followed by the cold interdiffusion of metal atoms between nanograins, a process known as cold welding. The sequence continues with fracture, leading to the formation of a nanostructure, which facilitates extended solid solubility. This is then followed by mechanical alloying, resulting in the formation of thermodynamically stable and/or metastable phases, and ultimately leads to amorphization.

Research has shown that mechanical alloying can produce amorphous phases in metals. However, differentiating between a "truly" amorphous material, an extremely fine-grained structure, and a composite containing very small crystals embedded within an amorphous matrix is challenging based solely on diffraction techniques. Only further studies such as neutron diffraction can conclusively verify whether the phases formed through mechanical alloying are truly amorphous. The milled powder is then subjected to heat treatment to attain the

intended microstructure and properties, with annealing promoting grain growth and the reduction of microstrain [104].

Nanocrystalline materials exhibit significantly distinct properties compared to both crystalline and amorphous materials, primarily due to their unique structure. This structure consists of extremely fine grains separated by what some researchers have described as "glass-like" disordered grain boundaries. The formation of the amorphous phase through mechanical alloying (MA) is attributed to a chemical solid-state reaction, believed to arise from the development of a multilayer structure during the milling process. When a mixture of elemental powders undergoes milling, the emergence of the amorphous phase is predominantly a result of the ultimate interdiffusion of atoms occurring at the newly created surfaces and interfaces. This interdiffusion is facilitated by defects and chemical disorder present within the crystalline structure [104].

A mixture of microcrystalline powders and various balls coated with hardened steel or tungsten carbide (WC) is placed in a sealed container and shaken. The ideal mass ratio of the balls to the mass of the powder is found to be 10:1.

Surface and interface contamination is a critical issue for all nanocrystalline materials produced through various synthesis techniques. During the mechanical attrition process, contamination from milling tools (especially iron) and atmospheric components (such as trace elements of O₂ and other rare gases) can arise. To minimize this, milling duration can be reduced and the purest, most ductile metal powder should be used. This approach allows a thin coating of the powder material on the milling tools, which significantly reduces iron contamination. Additionally, sealing the vial with a flexible "O" ring after loading the powder in an inert gas glovebox can help minimize or even eliminate atmospheric contamination[104], [105].

The cleanliness of the surfaces of nanocrystalline alloys produced via the mechanically alloying method was examined using X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Contamination from iron-based wear debris in mechanically synthesized nanomaterials can typically be minimized to less than 1–2%, while oxygen contamination can be reduced to below 300 ppm. Nevertheless, contamination from the milling atmosphere may positively influence the milling conditions when preparing metal or ceramic nanocomposites that involve a metallic element highly reactive with the gaseous or fluid environment. Conversely, a significant advantage of the top-down approach is the high production rates of nanopowders [106].

4.12.4 High energy ball mining

High-energy ball milling represents a top-down approach in nanotechnology for the synthesis of nanoparticles. In the HEBM process, significant force is exerted on the material, which can be either a pre-alloyed intermetallic or a solid chemical compound with a specific stoichiometry. This method

is recognized as a straightforward, efficient, and productive technique for generating a variety of nanopowders in mills. All else being equal, an increase in the intensity and duration of grinding, coupled with a reduction in the weight and size of the source powder particles, results in a smaller average size of the resulting powder particles. Additionally, as particle size decreases, grinding induces microdeformation within the crystallographic lattice of the material, with some energy being utilized to create microstresses that impede further grinding of the powder. Typically, the finest grinding results are obtained when utilizing a liquid milling medium [102].

The high-energy ball milling process subjects powder particles to significant energetic impacts. The mechanical alloying process can be categorized into four distinct stages: (i) the initial stage, (ii) the intermediate stage, (iii) the final stage, and (iv) the completion stage. i) In the initial stage of ball milling, powder particles experience flattening due to compressive forces resulting from the collisions of the milling balls. This micro-forging effect leads to alterations in the shapes of individual particles or clusters of particles that are repeatedly impacted by the high-kinetic-energy balls. ii) During the intermediate stage, the primary processes are fracturing and cold welding. While some dissolution may occur, the chemical composition of the alloyed powder remains heterogeneous. iii) In the final stage, the microstructure of the particles appears more homogeneous on a microscopic scale compared to the initial and intermediate stages, indicating that true alloys may have begun to form. iv) At the completion stage, the lamellar structures can no longer be resolved using optical microscopy. Any further mechanical alloying at this point will not enhance the dispersoid distribution. Consequently, a real alloy with a composition similar to that of the original constituents is formed [8], [9], [102].

The preparation of all nanocrystalline materials through the high-energy ball milling synthesis route presents several significant challenges, particularly concerning surface and interface contamination. In addition to this contamination issue, other drawbacks include extended processing times, a lack of control over particle morphology, the formation of agglomerates, and residual strain within the crystallized phase. Nevertheless, the high-energy ball milling process has garnered considerable attention and has inspired a wealth of research interest due to its promising outcomes, diverse applications, and potential scientific contributions. One of the most notable applications of high-energy ball milling is the synthesis of nanostructured metal oxides for gas detection [102].

4.12.5 Mechanochemical synthesis

Mechanochemical synthesis (MCS) can produce both stable and metastable phases in systems comprising two or more components. The MCS reaction involves the application of a strong mechanical force that leads to material breakdown and the formation of a new structure. This mechanochemical process is characterized as straightforward, environmentally friendly, and

cost-effective technology. A commonly used technique utilized in mechanochemical processes is the planetary ball mill, which operates by continuously revolving a large plate while simultaneously rotating the containers. The speeds of the plate's revolution (centrifugal) and the container's rotation (planetary) can be adjusted independently. During the grinding process, the collision of balls is crucial for transferring energy from the balls to the raw materials. As the raw materials absorb mechanical energy from the balls, their particles fracture, resulting in a reduction in particle size and an increase in specific surface area and surface energy. Furthermore, the products can be easily retrieved from the grinding machine. One of the most appealing aspects of the mechanochemical method is its simplicity in synthesizing nanostructured materials [102].

4.12.6 Hybrid properties

Numerous hydrogen storage systems have been developed to date, aiming to achieve the common goals for hydrogen storage materials:

- (i) cost-effectiveness,
- (ii) high volumetric and gravimetric density of hydrogen,
- (iii) rapid kinetics and suitable thermodynamic properties, and
- (iv) long-term cycling stability along with a high degree of reversibility.

Significant advancements in these properties have been made through chemical modifications and conventional thermal and mechanical processing methods. However, to this day, none of the known materials fully satisfy all the necessary properties for practical application. For instance, while the theoretical hydrogen storage capacity of LiBH_4 is 18 wt%, its high decomposition temperature restricts its usability. LaNi_5 , recognized for its excellent thermodynamic properties and rapid kinetics, is easy to activate but decomposes quickly at room temperature, offering only 1.4 wt% hydrogen storage capacity and lacking cost efficiency. In addition to the ongoing search for ideal new materials for hydrogen storage, researchers are also investigating various methods to enhance the properties of existing materials with potential [14], [107].

4.13 Hydrogen Storage Materials

Hydrogen storage materials can store hydrogen either as hydride or in its molecular form. Within the hydrides, three types of hydrogen atoms can be identified: protide (hydride) H^- , protium H^0 , and proton H^+ . Boron and aluminum create negatively charged molecular hydrides, such as BeH and AlH , which arise from their differing electronegativities. In contrast, carbon and nitrogen yield positively charged molecular hydrides. Transition metals like titanium, vanadium, zirconium, palladium, lanthanum, and cerium are known to form hydrides that include protium. These materials are classified as either solid or liquid. The theoretical packing density of equal spheres in both hexagonal close-packed (hcp) and face-centered cubic (fcc) structures is 74%, but this efficiency is reduced to approximately 40% to 50% in practical solid materials [74].

4.14 Hydrogen storage alloys

Metal hydrides (MH_x) have attracted considerable attention as a solution for hydrogen storage in a hydrogen economy. These materials, so-called "hydrogen storage alloys," are seen to reversibly absorb and desorb hydrogen at normal temperature and pressure conditions. They are thought to be one of the vital factors in overcoming energy-related and environmental problems. Other options for storing hydrogen include high-pressure gas cylinders and liquid hydrogen. A defining feature of metal hydrides is their exothermic absorption of hydrogen in select metals, enabling saturation capacities which can approach or even exceed that of liquid hydrogen. Researchers are hopeful that these compounds will yield increased hydrogen storage densities over pressurized tanks [108].

Hydrogen combines with many elements to give hydrides. The binary hydrides formed from these reactions can be divided into a few classes, which include:

- metal hydrides
- ionic hydrides (e.g. LiH)
- covalent molecular hydrides (for example, CH₄).

Figure 4.9 depicts all binary hydrides that may be produced by direct reaction of hydrogen with the metal.

The densities of hydrogen in most of these metal hydrides exceed those of liquid hydrogen (see following **Table 4.2**). The great majority of metallic Hydrides are prepared under normal temperature conditions using pure hydrogen.

Table 4.2 Hydrogen densities of some metal hydrides compared with liquid hydrogen.

Compounds	PdH _{0.8}	MgH ₂	TiH ₂	VH ₂	Liquid hydrogen
Hydrogen density (atom x 10 ⁻²² /cm ³)	4.7	6.6	9.2	10.4	4.2

Metallic hydrides

Metals forming hydrides for pressure higher then 0,1 MPa

Covalent hydrides

Ionic hydrides

IA	IIA																	IIIA
Li	Be																	Al
Na	Mg	IIIB	IVB	VB	VIB	VII B	VIII		IB	II B			VA					
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga						
Rb	Sr	Y	Zr	Nb	Mo	Tc		Rh	Pd		Cd	In	Sn					
Na	Ba	La	Hf	Ta								Tl	Pb					
		Ac																
		Ce	Pr	Nd		Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu			
		Pa	Th	U	Np	Pu	Am	Cm	Bk									

Figure 4.9 Alloys for hydrogen storage.

Alloys designed for hydrogen storage, which include hydride-forming transition metals labeled as A and non-hydride-forming metals identified as B, are regarded as highly effective materials for this purpose. LaNi₅ serves as a quintessential example of an AB₅ type hydrogen storage alloy. This alloy can reversibly retain 1.4 wt % of hydrogen when subjected to pressures ranging from 3 to 0.1 MPa at a temperature of 293 K, under a hydrogen dissociation pressure of 0.14 MPa. AB₅ type alloys find application as negative electrodes in nickel-metal hydride batteries. Alloys characterized by a body-centered cubic (BCC) structure possess a significant hydrogen density, with the alloy Ti_{0.22}Cr_{0.39}V_{0.39} (TieCreV) capable of absorbing and desorbing 2.2 wt % of hydrogen at 296 K. Nonetheless, at the lower temperature of 233 K, the absorption capacity drops to zero due to the low dissociation pressure.

A hydrogen storage alloy characterized by high dissociation pressure. The Ti_{1.1}CrMn (TieCreMn) alloy, classified as an AB₂ type, demonstrates remarkable hydrogen absorption and desorption capabilities at low temperatures, particularly when a portion of chromium is substituted with manganese. At 296 K, the Ti_{1.1}CrMn alloy exhibits a hydrogen capacity of 1.8 wt % within a pressure range of 33 MPa to 0.1 MPa. This capacity diminishes as the temperature decreases. At 233 K, the desorption capacity of H₂ at 0.1 MPa is recorded at 1.6 wt % with a dissociation pressure of 0.4 MPa. Additionally, the alloy (Ti_{0.7}Zr_{0.3})(Cr_{0.5}Fe_{0.5})₂ represents another category of AB₂ alloys with high dissociation pressure, which also reveals a significant reversible hydrogen capacity of 1.5 wt % at 233 K [87], [100], [106].

The densities of the hydrogen storage alloys designated as D can be determined using the following additive relationship.

$$D = \sum_{i=1}^n \frac{x_i M_i}{V} \quad \text{(Equation 4.1)}$$

$$V = \sum_{i=1}^n \frac{x_i M_i}{d_i} \quad \text{(Equation 4.2)}$$

A variety of chemical hydrides, including ionic, covalent, and complex hydrides made from light elements, are anticipated to achieve significant gravimetric and volumetric hydrogen densities ranging from 3 to 20 wt%. Most ionic and complex hydrides exhibit stability, with the exception of NaAlH₄. Research has indicated that MgH₂ functions as an intermediate hydride, bridging the gap between ionic and covalent hydrides. In contrast, covalent hydrides such as AlH₃ and NH₃BH₃ are characterized by their instability. The gravimetric hydrogen densities of these compounds tend to increase as their density decreases. Hydrogen desorption can occur through three primary methods: hydrolysis, ammonolysis, and thermolysis [108].

4.15 Intermetallic materials

A reinvigorated emphasis on hydrogen storage materials has arisen, encompassing

traditional metal hydrides to novel materials such as carbon nanostructures and innovative compounds. The conversion of the metal storage materials into their nanoparticulate forms confers two main advantages—one related to kinetics and another related to thermodynamics. The kinetic advantage is evident; nanoparticles allow for much more rapid rates of hydrogen absorption and desorption than that by the more commonly used microcrystalline particles. The thermodynamic advantage refers to the possibility of changing thermodynamic properties by manipulating particle size. Because the properties of sufficiently small particles are affected by such factors as surface energy and elasticity or plasticity effects, it becomes possible to alter the dissociation pressure of a substance by changing the particle dimensions [48].

In recent years, there has been a dramatic increase in academic interest in the study of nanostructured materials. This surge is driven mainly by advances in material synthesis and characterization techniques, along with the realization that such materials display a variety of intriguing and often unexpected properties, which could lead to a wide range of technological applications. For example, designed nanomaterials for hydrogen storage are crucial in the development of both storage and battery areas. Recent studies have shown that mechanical alloying (MA) of compounds such as TiFe, ZrV₂, LaNi₅, and Mg₂Ni considerably improves the initial hydriding rate. Such an improvement is attributed to a decrease in particle size as well as the formation of new, clean surfaces. In addition, La–Mg–Ni compounds with an A₂B₇ structure are being put into commercial use in the present Ni–MH_x batteries. Based on low-cost production and excellent discharge capacities over 300 mAh/g, La–Mg–Ni A₂B₇-type alloys are looked upon as very promising candidates for use as negative electrode materials in Ni–MH_x secondary batteries [57].

The intentional tailoring of microstructural properties via non-conventional processing techniques is expected to yield improved nanocrystalline intermetallics, which represent a new class of metal hydride materials. In fact, the classification of metal hydrides should be broadened to include hydrides based on intermetallic compounds of transition metals besides binary systems. Numerous alloys have been proposed for their possible applications as hydrogen storage materials, including those obtained from rare earth elements (RE) with nickel (AB₅-type), alloys based on zirconium and vanadium with nickel (AB₂-type) and alloys of titanium and magnesium with nickel (AB- or A₂B-type).

Table 4. 3 *Hydrides of binary intermetallic compounds.*

Hydrides	System
TiFeH ₂	AB
ZrV ₂ H _{5.5}	AB ₂
LaNi ₅ H ₆	AB ₅
Mg ₂ NiH _{3.6}	A ₂ B

Table 4. 4 Hydride-forming alloys.

Alloy and structure	Hydrides	Type of alloy
ZrV ₂ -cubic	ZrV ₂ H _{5.5}	AB ₂
LaNi ₅ -hexagonal	LaNi ₅ H ₆	AB ₅
TiFe-cubic	TiFeH ₂	AB
Mg ₂ Ni-hexagonal	Mg ₂ NiH ₆ (at 350° C)	A ₂ B
La _{0.8} Mg _{0.2} Ni _{3.75} -hexagonal	(La,Mg) ₂ Ni ₇ H	A ₂ B ₇

In each of these alloys, component A is the one which forms stable hydride.

Component B has some other roles:

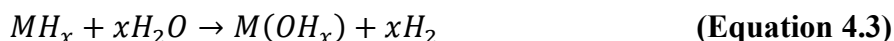
- It can serve as a catalyst to enhance the hydriding-dehydriding kinetic characteristics,
- It can alter the equilibrium pressure of the hydrogen absorption-desorption reaction to a suitable value,
- It can also increase the stability of the alloy, inhibiting the dissolution or the formation of a compact oxide layer of component A.

The TiNi, ZrV₂, and LaNi₅ phases are some well-known materials which have relatively large hydrogen absorption capacity at relatively mild temperature and pressure conditions. In recent years, these hydrogen-absorbing compounds have appeared as promising candidates for applications as negative electrode materials in rechargeable nickel-metal hydride batteries. Also, magnesium-based hydrogen storage alloys have been investigated as electrode materials for Ni-MH batteries. The substitution of B in the AB₅ structure (La (Ni_{1-x}M_x)₅, M = Co, Cu, Fe, Mn, or Al) by Ni is necessary to retain the hydrogen absorption capacity. The addition of Co also reduces the volumetric expansion upon the hydriding reaction and eases the rise in internal cell pressure; on the other hand, it leads to an increase in the overall alloy cost. The substitution of Co with Fe can reduce the cost without sacrificing the cell performance and diminish the decrepitation of the alloy upon hydriding. Al substitution increases the energy needed to form the hydride while Mn decreases the equilibrium pressure without a significant reduction in hydrogen storage capacity. Finally, V expands the lattice and improves hydrogen diffusion [106], [109].

4.16 Hydrolysis and ammonolysis of chemical hydrides

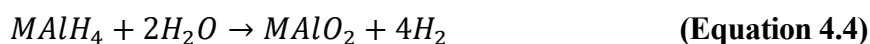
The hydrolysis of lightweight hydrides, which include chemical hydrides such as ionic, complex, and covalent hydrides, that contain protide H⁺ or negatively charged molecular hydrides, produces significant quantities of hydrogen at ambient temperature. Ionic hydrides can undergo

hydrolysis to produce hydrogen gas (H₂) and hydroxides, as represented by the following equation.



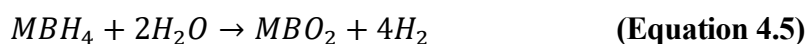
M: Li, Na, Ca, Mg, x:1(Li, Na), x:2(Mg, Ca)

Sodium hydride (NaH), lithium hydride (LiH), and calcium hydride (CaH₂) exhibit vigorous reactions with water, achieving conversion rates exceeding 90% within one minute. In contrast, the hydrolysis of magnesium hydride (MgH₂) occurs at a significantly slower rate due to the formation of an insoluble layer of magnesium hydroxide (Mg(OH)₂). It has been observed that the yield of hydrogen gas from this hydrolysis can be enhanced using acetic acid and a catalyst. Additionally, high-pressure hydrogen, exceeding 4 MPa, can be produced by milling MgH₂ in conjunction with the addition of niobium pentoxide (Nb₂O₅). Furthermore, alanates such as lithium aluminum hydride (LiAlH₄) and sodium aluminum hydride (NaAlH₄) can react vigorously with water under standard pressure and temperature conditions [110].



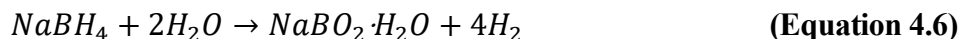
M: Li, Na

At standard temperatures, minimal quantities of hydrogen gas (H₂) are released when lithium borohydride (LiBH₄) and sodium borohydride (NaBH₄) are combined with water. It has been established that the hydrolysis reactions of these borohydrides can be enhanced using catalysts, including cobalt chloride, nickel chloride, ruthenium supported on ion exchange resin beads, fluorinated metal hydrides, Raney nickel, and PteLiCoO₂, among others. The theoretical framework for the hydrolysis reaction is represented by the following equation.

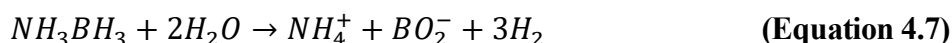


M: Li, Na

In the absence of catalysts, the production of hydrogen gas (H₂) increases gradually over time, ultimately reaching a stable conversion rate of 7% due to the rising pH of the solution. In contrast, the hydrogen generation rates when utilizing PteLiCoO₂ and PteCoO catalysts remain constant and are not influenced by time. Notably, the PteLiCoO₂ catalyst achieves the complete stoichiometric generation of H₂ within 15 minutes. Furthermore, these catalysts are not consumed during the hydrolysis process, allowing for their reuse. The X-ray diffraction intensity curve of the byproduct reveals that the diffraction peaks correspond to NaBO₂·2H₂O. Consequently, the practical reaction can be approximate as follows [21], [110].



The gravimetric and volumetric hydrogen densities associated with this reaction are measured at 5.3 wt% and 5.4 kgH₂/100 L, respectively, when accounting for the weight of water. A hydrogen generator designed for a 10 kW scale, utilizing the hydrolysis reaction of sodium borohydride (NaBH₄), has been developed. The gravimetric and volumetric hydrogen densities of this generator, which includes both the fuel tank and the byproduct tank, are recorded at 1.3 wt% and 0.5 kgH₂/100 L, respectively. Additionally, ammonia borane can react with water to produce hydrogen according to the specified equation [47].



Catalysts that are both efficient and cost-effective have been developed to enhance the kinetic properties under moderate reaction conditions. **Figure 4. 10** illustrates the calculated theoretical gravimetric and volumetric hydrogen densities of chemical hydrides considering the weight of water. The calculations assume a packing ratio of 50% for the chemical hydride and 100% for water. The gravimetric hydrogen densities for the chemical hydride-water systems range from 5 to 14 wt%. Additionally, the volumetric hydrogen densities of certain chemical hydrides exceed that of liquid hydrogen (7.08 kg/100 L). The hydrogen generation reaction is exothermic, with standard heat of formation values ranging from -83.5 to -139 kJ/mol for ionic hydrides, -125 to -136 kJ/mol for alanates, -54.1 to -67.4 kJ/mol for borohydrides, and -52 kJ/mol for NH₃BH₃. This suggests that the byproducts, including [M(OH)_x, MAIO₂, MBO₂, NH₄BO₂], cannot be reversed through hydrogen pressure treatment [12].

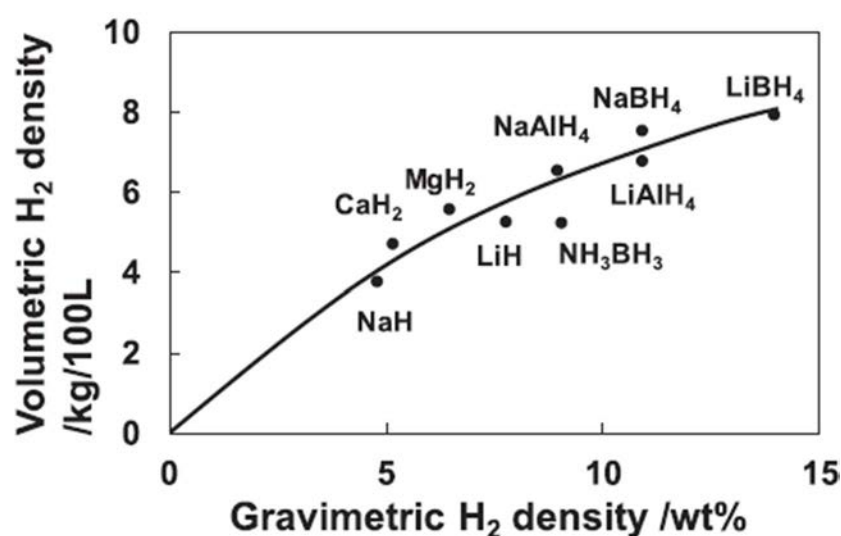


Figure 4. 10 The volumetric hydrogen densities of certain chemical hydrides [88].

4.17 Thermolysis of chemical hydrides

4.17.1 Alanates

In 1997, Bogdanovic and colleagues indicated that the reversible hydrogen desorption reaction of NaAlH₄ could be enhanced through the incorporation of small quantities of Ti-based catalysts, including TiCl₃. The theoretical gravimetric hydrogen density for this process is 5.6 wt%, with a volumetric hydrogen density of 3.5 kgH₂ per 100 liters and a packing density of 0.62 g/cm³ [108].

$$\Delta H_0: -37 \text{ kJ/mol } H_2 (NaAlH_4 \leftrightarrow 1/3 Na_3AlH_6 + 2/3 Al + H_2) \quad (\text{Equation 4.8})$$

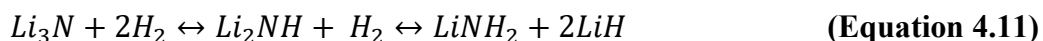
$$\Delta H_0: -47 \text{ kJ/mol } H_2 (1/3 Na_3AlH_6 + 2/3 Al \leftrightarrow NaH + Al + 1/2 H_2) \quad (\text{Equation 4.9})$$

$$\Delta H_0: -35 \text{ kJ/mol } H_2 (NaAlH_4 \leftrightarrow NaH + Al + 1/2 H_2) \quad (\text{Equation 4.10})$$

4.17.2 Borohydrides

Compound LiBH₄ demonstrates a reversible process, resulting in the formation of LiH and B. It is capable of absorbing hydrogen at 963 K and 20 MPa, leading to the synthesis of LiBH₄. The desorption reactions of hydrogen from borohydrides are highly appealing for hydrogen storage solutions, given their theoretical hydrogen density surpassing 9.6 wt%. These borohydrides are classified as stable complex hydrides, supported by their standard heat of formation metrics.

In their research, Chen et al. examined the hydrogen absorption capabilities of lithium nitride (Li₃N), identifying it as a viable hydrogen storage material and outlining the associated reaction involving Li₃N [111].



The reversible hydrogen storage densities are 11.5 wt% and 7.35 kgH₂/100 L at the packing density of 0.635 g/cm³,

$$\Delta H_0: 81 \frac{\text{kJ}}{\text{mol}} H_2 (Li_3N + 2H_2 \leftrightarrow LiNH_2 + 2LiH) \quad (\text{Equation 4.12})$$

4.17.3 Alane

Aluminum hydride, commonly referred to as "alane," is a notable covalent hydride for hydrogen storage, boasting a substantial hydrogen capacity of 10.1 wt% (7.47 kgH₂/100 L). Nevertheless, AlH₃ exhibits thermodynamic instability, with a standard enthalpy change of $\Delta H_0 = -6.6 \text{ to } -7.6 \text{ kJ/mol } H_2$. To achieve reversibility, it necessitates hydrogen pressures on the order of gigapascals [112].

4.17.4 NH₃BH₃

Ammonia borane (NH₃BH₃) is a promising substance due to its high theoretical hydrogen capacity of 19.6 weight percent, with a volumetric hydrogen density of 7.64 kgH₂ per 100 liters and a packing density of 0.39 g/cm³. Following the desorption of hydrogen from ammonia borane, the

resultant spent fuel, known as polyborazylene, can be reconstituted into ammonia borane using hydrazine in a liquid ammonia environment. Various ammonia borane-derived materials have been synthesized, including LiNH_2BH_3 (with a hydrogen capacity of 10.9 wt%), NaNH_2BH_3 (7.5 wt%), and $\text{NaHeNH}_3\text{BH}_3$ (5.2 wt%). The standard heat of formation for these amidoboranes ranges from 3 to 5 kJ/mol H_2 [101].

4.17.5 Nano-composite materials

The high operational temperatures associated with chemical hydrides, resulting from their slow reaction rates (due to high activation energy) and the complexities in controlling thermodynamic stability (ΔH_0), pose significant limitations on the practical application of chemical hydride systems. These limitations can be mitigated by the development of nanocomposite materials. As depicted in next **Figure 4. 11**, a design framework for nanocomposite materials aimed at hydrogen storage is presented. These materials integrate a catalyst and composite chemical hydrides at the nanoscale. The presence of the catalyst enhances the reaction rate by enabling a different mechanism that requires lower activation energy. Moreover, the thermodynamic stability of the nanocomposite materials, including the standard enthalpy difference (ΔH_0) and standard entropy difference (ΔS_0), can be fine-tuned through the combination of various chemical hydrides. The nanoscale effects also contribute to improved kinetics for hydrogen absorption and desorption, which may lead to alterations in the thermodynamic stability of the materials. A variety of nanocomposite materials have been produced utilizing the mechanical milling method.

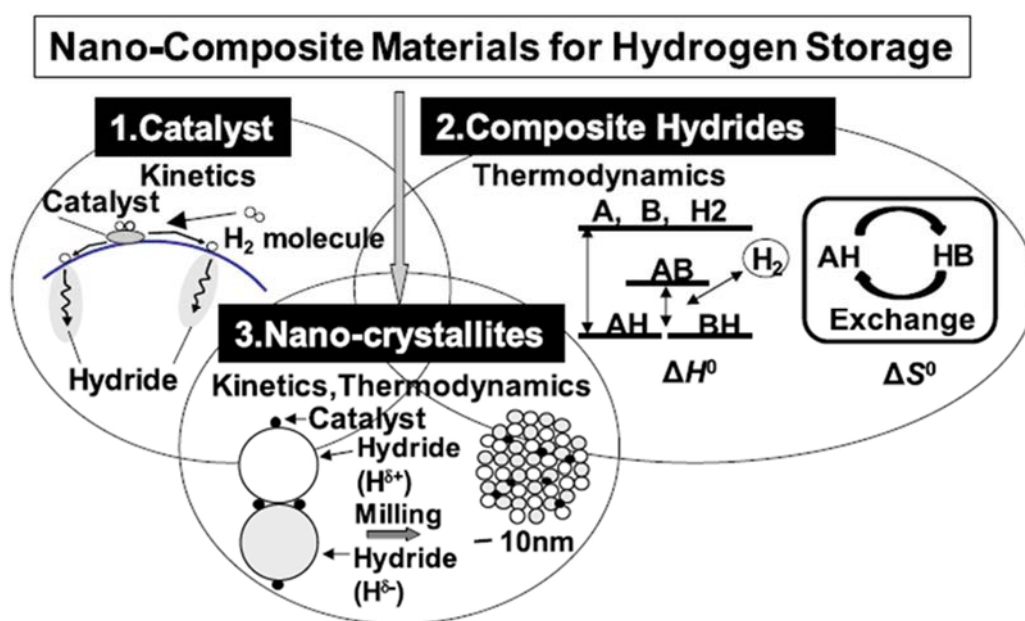


Figure 4. 11 Design concept of nano-composite materials for hydrogen storage[112]

4.17.5.1 Mg-based nanocomposite materials

Magnesium-based nano-composite materials incorporating nickel and niobium pentoxide as

catalysts exhibit remarkable kinetics for hydrogen absorption and desorption. Following hydrogen desorption at 493 K, the nanocomposite containing niobium pentoxide is capable of absorbing hydrogen even at 223 K under a pressure of 1 MPa. In contrast, the hydrogen absorption capacity of pure magnesium remains below 0.1 wt % at ambient temperature. The standard heat of formation for these nano-composite materials is reported to be approximately -76 kJ/mol H₂, which is consistent with the value for magnesium, recorded at -75.3 kJ/mol H₂ [99].

Li – N - H system

The Li-N-H system doped with TiCl₃ functions as a catalyst that facilitates reversible hydrogen absorption and desorption. The standard heat of formation (ΔH_0) for the LiNeH system is determined through Pressure-Composition-Temperature (PCT) and differential scanning calorimetry (DSC) measurements [21].

Li – Mg - N - H system

Three distinct types of Li-Mg-N-H systems (Mg(NH₂)₂eLiH) have been independently documented by researchers including Luo , Xiong et al. , Leng et al. , and Nakamori et al. [113]. The standard heat of formation for these systems ranges from -42 to -46 kJ/mol H₂, while the reversible hydrogen density is reported to be between 5.2 and 5.5 wt% (equivalent to 6 to 7 kg H₂ per 100 L). The particle size within the Li-Mg-N-H system is approximately ten nanometers. Furthermore, the kinetics of the system is enhanced through the incorporation of 3 mol% KH [87].

Li – Ca - N - H system

The Li-Ca-N-H system, represented as Ca (NH₂)₂ + 2LiH, exhibits the ability to reversibly absorb and desorb hydrogen under conditions of elevated H₂ pressure. The standard enthalpy of formation for this system is measured at -46 kJ/mol H₂, while the reversible hydrogen density is recorded at 4.5 wt%, equivalent to 3.2 kg H₂ per 100 liters.

Li – Ca - H system

The synthesis of the hydrogenated graphite and LiH composite (Li-C-H system) is achieved through the ball-milling of both materials. The Li-C-H systems are capable of reversibly storing 4.5 wt% of hydrogen at a temperature of 623 K and a pressure of 3 MPa for a duration of 8 hours, resulting in a reversible hydrogen density of 4.5 wt% or 2.3 kgH₂ per 100 liters.

Li – Al - N - H system

The composites formed through the combination of LiAlH₄ or Li₃AlH₆ with LiNH₂ systems

have been documented by Kojima et al., Xiong et al., Lu et al., and Nakamori et al. [110] Following the initial desorption of hydrogen, the hydrogen absorption and desorption capacities of the composite, which includes a nano-Ni catalyst, demonstrate values ranging from 3.0 to 4.0 wt% under hydrogen pressures of 10 to 0.004 MPa at temperatures between 473 and 573 K [114].

Li – Mg - B - H system

Vajo et al. effectively illustrated the destabilization of LiBH_4 through the incorporation of MgH_2 as an additive. The composite, which is doped with TiCl_3 , is produced via ball-milling and exhibits a reversible hydrogen absorption/desorption capacity ranging from 8.0 to 10.0 wt% [30], [81].

4.17.6 Carbon materials

Materials characterized by an exceptionally high specific surface area exhibit significant potential for hydrogen storage applications. The gravimetric hydrogen densities of various carbon nanostructures are illustrated in relation to their specific surface area in next **Figure 4. 12**. The relationship between specific surface area and hydrogen adsorption capacity indicates that an increase in the Brunauer-Emmett-Teller (BET) surface area correlates with enhanced hydrogen absorption for activated carbon, single-walled carbon nanotubes (SWNT), and graphite nanofibers (GNF). Superactivated carbon, with a specific surface area of approximately $3000 \text{ m}^2/\text{g}$, is capable of reversibly adsorbing and desorbing 5 wt % of hydrogen at 77 K and 1.3 wt % at 296 K. However, the volumetric hydrogen density at 77 K is limited to $1.5 \text{ kg H}_2/100 \text{ L}$ due to a low packing density of $0.3 \text{ g}/\text{cm}^3$. The adsorption isotherm conforms to a Langmuir-type equation, with values surpassing those of traditional activated carbon, SWNT, and GNF. According to the Clausius-Clapeyron equation, the heat of adsorption (standard heat of formation) for superactivated carbon is estimated at approximately $-6 \text{ kJ}/\text{mol H}_2$, indicating instability at room temperature. At 20 K, the gravimetric and volumetric hydrogen densities of superactivated carbon are 10 wt % and $7.5 \text{ kg H}_2/100 \text{ L}$, respectively [21].

4.17.7 Liquid Hydrides

Ammonia, represented by the chemical formula NH_3 , is classified as a hydride. It possesses a high gravimetric hydrogen density of 17.8 wt%, with a density of $0.682 \text{ g}/\text{cm}^3$ at 0.1 MPa and 240 K, and $0.603 \text{ g}/\text{cm}^3$ at 1 MPa and 298 K. Additionally, in its liquid state, NH_3 exhibits a significant volumetric hydrogen density ranging from 10.7 to 12.1 kgH_2 per 100 liters. Methyl-cyclohexane (C_7H_{14}) is another viable liquid hydride, offering a moderate hydrogen storage density of 6.2 wt% and 4.7 kgH_2 per 100 liters. This compound can be used as a liquid fuel like gasoline under standard conditions, facilitating the material transfer process. However, for the complete hydrogen transportation cycle, toluene, which is produced through the dehydrogenation of C_7H_{14} , must be transported back to the hydrogen production site. Hydrous hydrazine, a liquid with a hydrogen content of 8.1 wt% and 8.3 kgH_2 per 100 liters, is also a promising candidate for hydrogen generation under ambient conditions.

Formic acid, another liquid hydride, contains hydrogen at levels of 4.4 wt% and 5.3 kgH₂ per 100 liters. Consequently, the hydrogen densities of liquid hydrides range significantly from 4.4 to 17.8 wt% and from 5.3 to 12.1 kg H₂ per 100 liters. In the following **Figure 4. 12**, hydrogen storage properties of ammonia, formic acid, methyl-cyclohexane and hydrous hydrazine [115].

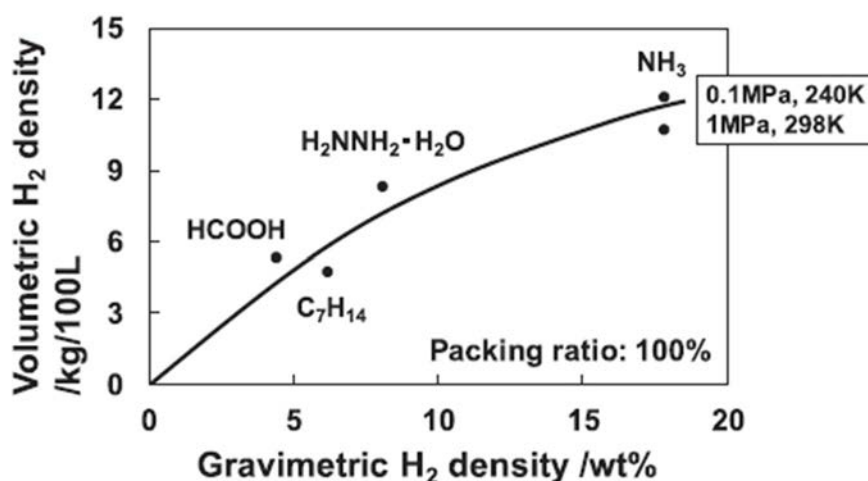


Figure 4. 12. Calculated hydrogen storage properties of liquid hydrides (ΔH_0 of HCOOH: -31.6 kJ/molH₂, ΔH_0 of C₇H₁₄: -67.5 kJ/molH₂, ΔH_0 of H₂NNH₂: 25.3 kJ/molH₂, ΔH_0 of NH₃: -30.6 kJ/molH₂)

Like other fuels, the application of hydrogen mandates compliance with safety regulations, which are detailed in the EU safety sheets.

- S9: keep containers in a well-aired location
- S16: keep away from ignition sources – do not smoke (explosion areas)
- S33: take precautions against electrostatic charge.

Due to the lightweight and highly diffusive nature of hydrogen gas, it is generally straightforward to avert explosive concentrations by ensuring proper ventilation. When it comes to the storage of compressed hydrogen gas (CGH₂), adherence to pressure vessel regulations is essential. Additionally, direct exposure to cryogenic liquids and gases poses a significant risk of severe frostbite or frozen burns. Moreover, hydrogen exposure can result in embrittlement and diffusion with various materials, including many plastics and mild steel, potentially leading to fractures and leaks [21].

4.17.8 One dimensional carbon materials

Linear carbon, also referred to as long linear carbon atomic chains, represents a category of one-dimensional carbon materials, with carbon nanotubes and carbon nanofibers serving as prime examples. These materials are characterized by their high aspect ratios, exceptional strength, superior electrical conductivity, and remarkable thermal conductivity. Their elongated, filament-like structure contributes to their widespread use in reinforcement materials and conductive applications. Notable

instances of these materials include carbon nanotubes and carbon nanofibers [21].

4.17.9 Carbon nanotubes

Carbon nanotubes (CNTs) are nanoscale tubular structures formed when carbon atoms bond, resulting in a hexagonal lattice configuration. Their exceptional thermal stability and distinctive hollow architecture make them ideal for use in magnesium-based hydrogen storage materials [21].

Understanding the catalytic function of single-walled carbon nanotubes (SWNTs) in augmenting the hydrogen storage capacity of MgH_2 was significantly advanced by Cheng et al. [47]. They developed a composite material that could quickly release 6 weight percent H_2 at 350 degrees Celsius in 5 minutes and absorb 6 weight percent H_2 at 200 degrees Celsius in 10 minutes in a hydrogen environment with 2 MPa. As opposed to 126 ± 3 kJ/mol for pure MgH_2 , the activation energy needed for hydrogen release was greatly reduced to 96 ± 1 kJ/mol. In a follow-up study by the same team, the composite successfully demonstrated the synergistic catalytic effect of SWNTs and NbF_5 by releasing roughly 4 weight percent H_2 at 300 °C in 15 minutes and absorbing 5.2 weight percent H_2 at 100 °C in 10 minutes under a 2 MPa hydrogen atmosphere. Additionally, the addition of NbF_5 not only improves the kinetics of MgH_2 , but it may also make it easier for fluorine ions to partially replace hydrogen ions in MgH_2 , forming $\text{MgH}_2\text{-xFx}$ solid solutions that alter the material's thermodynamic stability [116], [117].

According to theoretical calculations and experimental studies by Tortoza et al. [108], the Mg-H-F system can form $\text{MgH}_2\text{-xFx}$ solid solutions with a variety of compositions. Compared to MgH_2 , these solid solutions—especially those with higher fluorine contents—show better thermodynamic stability, requiring higher temperatures for hydrogen release. A systematic analysis of the structural alterations and hydrogen storage properties of $\text{MgH}_2\text{-xFx}$ solid solutions made by ball milling MgH_2 and NbF_5 was conducted by Pighin et al. [118]. They found that the initially separate hydrogen-rich and fluorine-rich solid solutions gradually blend into a single $\text{MgH}_{1.60}\text{F}_{0.40}$ solid solution after many millings. The solid solution that is rich in hydrogen undergoes most of the processes of hydrogen release and absorption, while the solid solution that is rich in fluorine holds steady. Consequently, the formation of $\text{MgH}_2\text{-xFx}$ solid solutions not only mitigates the agglomeration and growth of Mg/MgH_2 particles, thereby enhancing kinetics, but also increases thermodynamic stability, which influences the complete dehydrogenation and reversible capacity to a certain degree [21].

The alteration of MgH_2 through the incorporation of NbF_5 as an additive encompasses the synergistic influence of various factors. Firstly, the NbH phase generated from the reaction may serve as a "gateway" for hydrogen storage, thereby facilitating the kinetics of hydrogenation and dehydrogenation in MgH_2 . Secondly, the introduction of fluorine ions results in the creation of $\text{MgH}_2\text{-xFx}$ solid solutions, which, while advantageous for the dispersion of the Mg phase and the

enhancement of kinetics, simultaneously contributes to an increase in the thermodynamic stability of the material.

The use of carbon nanotubes (CNTs) as additional additives has been investigated by researchers after considering these factors. In this context, Yao et al. [119] made a notable advancement by utilizing 0.5 wt.% CNTs alongside a 4.5 wt.% vanadium-based complex as a catalyst. This combination demonstrated exceptional hydrogen absorption characteristics, rapidly absorbing 6.50 wt.% H_2 at 200 °C and 2 MPa hydrogen pressure within just 1 minute, while achieving complete desorption within 10 minutes at 300 °C. Importantly, the inclusion of CNTs and the vanadium-based complex resulted in a decrease of approximately 7 kJ/mol H_2 in desorption enthalpy compared to pure MgH_2 . In a similar vein, when 5 wt.% ZrO_2 and 5 wt.% CNTs were ball milled with MgH_2 , the resulting composite exhibited remarkable hydrogen release performance, releasing 6.24 wt.% of H_2 at 300 °C in 15 minutes. Additionally, at 150 °C and 3 MPa hydrogen pressure, it effectively absorbed around 6.73 wt.% H_2 in 2 minutes. Notably, even at room temperature (25 °C), the composite was capable of absorbing approximately 4.0 wt.% of H_2 in about 10 minutes [116], [117].

It must be pointed out that the catalytic effect of CNTs is pronounced when used together with bimetallic complexes, especially in the case of MgH_2 . In a study of Han et al. [120] NiFe nanoparticles were deposited on the surface of CNTs, followed by its co-milling with MgH_2 . In the next figures both (a) and (b) are represented the resulting NiFe@CNT of a SEM composite and TEM composite, respectively. **Figure 4. 13** (c) presents the elemental distribution that further confirms the homogeneous distribution of NiFe within the CNTs [120].

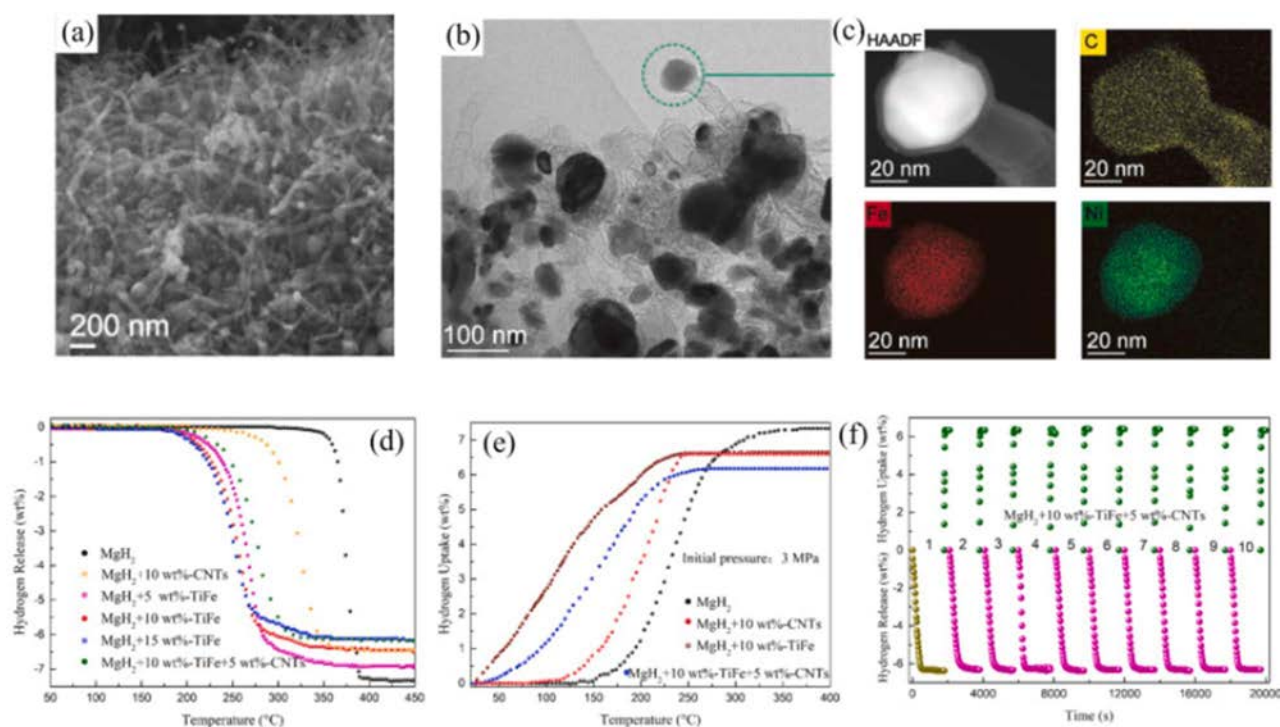


Figure 4. 13 NiFe@CNT images of (a) SEM, (b) TEM, and (c) elemental mappings [120]; Composites non-isothermal curves of (d)desorption and (e) absorption, (f) Cycling curves $MgH_2 + 10$ wt.%-TiFe + 5 wt.%-CNTs [21].

The MgH₂–NiFe@CNT composite exhibited a significant hydrogen absorption of 4.06 wt.% in XX min at 100 °C, and 3.25 wt.% in XX min at 75 °C. For comparison, pure ball-milled MgH₂ hardly absorbed hydrogen even at 150 °C. The MgH₂–NiFe@CNT composite also exhibited a much lower initial desorption temperature of 225 °C, which was 122 °C lower than that of MgH₂. Moreover, the activation energy necessary for dehydrogenation was also significantly lowered, from 151.8 kJ·mol^{−1} to 49.7 kJ·mol^{−1}. Such outstanding hydrogen storage behavior of MgH₂–NiFe@CNT composite was caused by synergetic effects: Mg₂Ni/Mg₂NiH₄ worked as "hydrogen pump," and α-Fe served as a "hydrogen channel." Besides, the beneficial dispersion effect supplied by CNTs boosted its overall performance. The MgH₂–TiFe–CNTs composite also shows excellent hydrogen storage properties, as shown in **Figure 4. 13d–f**. The addition of 10 wt.% TiFe nanoparticles significantly lowers the onset dehydrogenation temperature of MgH₂, showing much better catalytic activity than 10 wt.% CNTs (**Figure 4. 13d**). Further increasing the content of TiFe to 15 wt.% does not decrease the onset temperature further and results in a slower dehydrogenation rate at 275 °C [21].

The composite with 10 wt.% TiFe and 5 wt.% CNTs exhibits a slightly increased onset temperature compared to the sample with 10 wt.% TiFe alone, while the dehydrogenation rate is kept constant until the full release of hydrogen is reached. About hydrogen absorption, the composite of MgH₂+10 wt.% TiFe+5 wt.% CNTs starts hydrogen absorption at 40 °C, which is higher than 25 °C observed for the MgH₂+10 wt.% TiFe composite. In addition, the MgH₂+10 wt.% TiFe composite suffers from an 8% loss of hydrogen capacity, decreasing from 6.3 wt% to 5.8 wt.% after 10 cycles. In contrast, the MgH₂+10 wt.% TiFe+5 wt.% CNTs composite shows a stable capacity of 6.3 wt.% for 10 cycles with almost no significant degradation. The above results indicate that even though CNTs may be less effective than TiFe in improving the thermodynamic properties of MgH₂, they are very important in maintaining the cycle stability of the composite [21].

In addition to their function as catalysts in conjunction with transition metals, carbon nanotubes (CNTs) can act as structural materials for encapsulating magnesium hydride (MgH₂) within nanostructures. This process entails a wet impregnation technique, where MgH₂ is deposited onto CNTs, followed by compression at an exceptionally high pressure of 750 MPa. In this scenario, CNTs create adequate spatial barriers that hinder the growth and clustering of MgH₂ nanoparticles, while promoting fine particle sizes and a uniform distribution of MgH₂, thus improving hydrogen storage capabilities. Consequently, the resulting composite materials exhibit particle sizes between 15 and 20 nm and a loading capacity of 76.8%. Upon heating to 300 °C, the composite can release 5.7 wt.% of hydrogen over a period of 60 minutes and can absorb the same quantity of hydrogen at 275 °C under a pressure of 8 MPa within 10 minutes. Wu et al. [116] utilized mechanical ball milling to encapsulate MgH₂ within CNTs, leveraging the confining and catalytic characteristics of nickel-doped CNTs, which may enhance hydrogen diffusion, prevent the aggregation of magnesium and magnesium hydride, and significantly lower the dehydrogenation activation energy to 74.8 kJ·mol^{−1} [21], [117].

This composite demonstrated remarkable hydrogen release properties, yielding 7.29 wt.% H₂ within 60 minutes at a temperature of 250 °C, and attained a significant hydrogen absorption rate of 7.20 wt.% in just 30 minutes at 200 °C. Additionally, MgH₂@Ni-CNTs exhibited outstanding cyclic stability over ten cycles, showing no considerable loss in capacity. Nevertheless, it is crucial to recognize that maintaining stable MgH₂ confinement within carbon nanotubes through mechanical ball milling may present certain challenges due to inherent limitations [21], [117].

4.17.10 Carbon nanofibers

Carbon nanofibers (CNFs) are primarily composed of graphene layers that are stacked and oriented at different angles along the axis of the fiber, resulting in a honeycomb-like structure. This unique material, which combines characteristics of both CNFs and traditional fibers, shows significant potential in catalysis owing to its dense structure and elevated specific surface area [117].

ball milling on MgH₂ combined with 5 wt.% carbon nanofibers (CNFs) was performed in a study of Lillo-Ródenas et al. [121], resulting in a composite that can release approximately 5 wt.% hydrogen within 20 minutes at a temperature of 300 °C. This release time was shortened by 220 minutes compared to ball-milled MgH₂ without the addition of CNFs, and the performance remained consistent over five cycles. This improvement is attributed to the CNFs, which effectively prevented the aggregation and growth of Mg/MgH₂ particles. Shahi et al. [122] noted that the catalytic influence of CNFs on MgH₂ was dependent on their morphological characteristics. The composite containing helical carbon nanofibers (HCNFs) exhibited a higher hydrogen release rate at 300 °C, leading to a temperature decrease of 34 °C in comparison to porous CNFs (pCNFs). This temperature reduction was even more pronounced, reaching 67 °C, when contrasted with pure ball-milled MgH₂. Under a hydrogen atmosphere of 20 MPa at 300 °C, around 5.5 wt.% hydrogen within 15 minutes was absorbed by the MgH₂-HCNFs composite, while only 5 wt.% hydrogen was absorbed by the MgH₂-PCNFs. This variation in performance is likely due to the greater specific surface area of HCNFs, which offers more nucleation sites for Mg/MgH₂ [21].

The incorporation of 10 wt.% carbon fibers (CFs) during the ball milling of MgH₂ was demonstrated in the study of Bobet et al. [123] and this resulted in an increase in hydrogen release at 330 °C from 4.4 wt.% (achieved with MgH₂ alone) to 5.8 wt.%. Additionally, under a hydrogen atmosphere of 300 °C and 1 MPa, the hydrogen absorption improved from 4.6 wt.% to 5.3 wt.%. The fact that carbon nanofibers (CNFs) could enhance the efficiency of ball milling was revealed, thereby reducing the size of the particles of MgH₂ without altering the phase composition of Mg/MgH₂. Moreover, the presence of CNFs was found to promote a more uniform distribution of MgH₂. This leads to prevention of aggregation and growth of Mg/MgH₂ particles during the reaction [116].

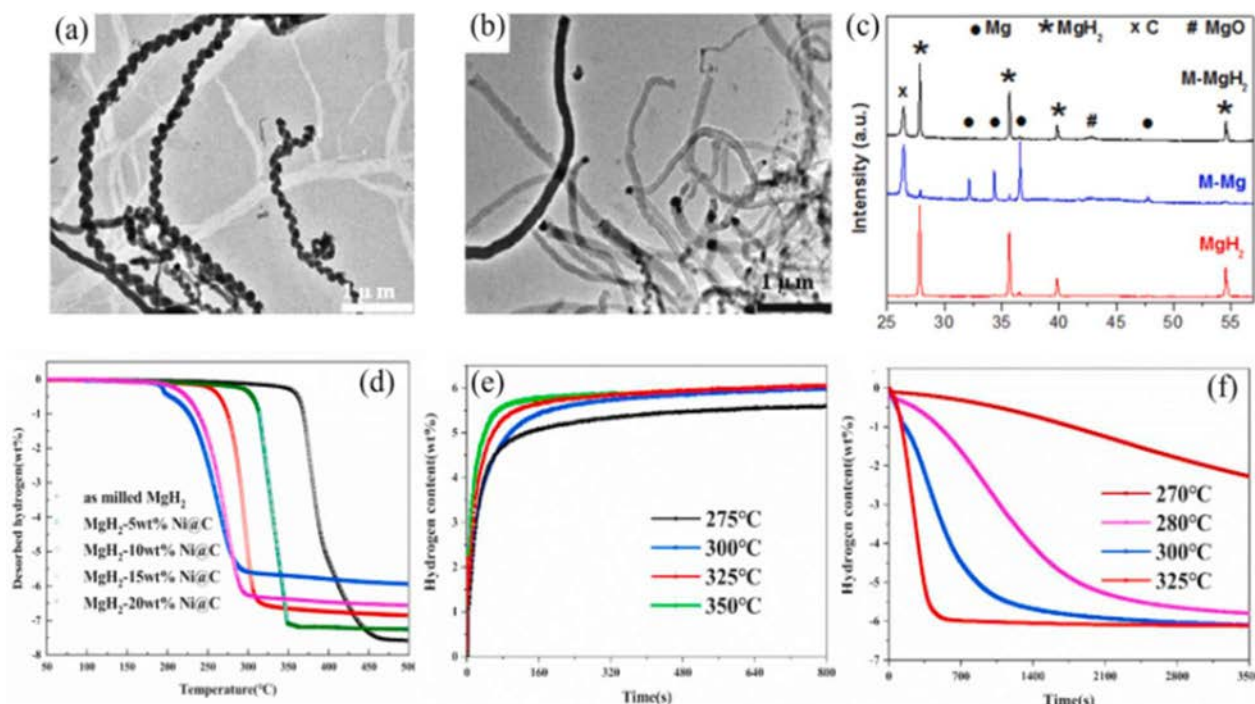


Figure 4. 14 SEM images of (a) HCNFs (b)PCNFs; (c) Composites XRD ; (d) Composites Temperature-programmed desorption (TPD) curves, (e) Hydrogen absorption and desorption (f) kinetics curves of MgH₂-10 wt.% Ni@C[21]

Ball milling on a composite consisting of 10 wt.% Ni nanoparticles encapsulated in carbon nanofibers (CNFs) along with MgH₂ was executed in the study of Yu et al. [104] in order to improve kinetic performance. The resulting MgH₂-10 wt.%Ni@C composite began hydrogen release at 250 °C, reaching its maximum at 350 °C. It demonstrated a hydrogen absorption capacity of 6.0 wt.% at 300 °C under a 3 MPa hydrogen atmosphere, and a maximum hydrogen desorption capacity of 5.79 wt.% at 280 °C. In comparison, pure MgH₂ required a temperature of 350 °C to release a similar quantity of H₂. The activation energy for dehydrogenation was significantly reduced from 187.41 kJ/mol for MgH₂ to 93.08 kJ/mol for the composite. Dibutylmagnesium was used in the study of Zou et al. [124] as a precursor to load MgH₂ onto Ni@pCNFs via wet impregnation and hydrogenation, resulting in the MgH₂/Ni@pCNFs composite. This composite could release 4.1 wt.% H₂ and absorb 4.3 wt.% H₂ within 10 minutes at 250 °C and a 3 MPa hydrogen atmosphere, when the temperature goes to 300 °C. This notable enhancement is attributed to the catalytic effect of Ni nanoparticles and the confinement provided by pCNFs. Due to that, the dehydrogenation activation energy from $142.27 \pm 7.79 \text{ kJ} \cdot \text{mol}^{-1}$ (for pure MgH₂) to $96.58 \pm 4.16 \text{ kJ} \cdot \text{mol}^{-1}$ was reduced [21].

Furthermore, the partial confinement of Ni and MgH₂ by pCNFs may lead to a certain level of aggregation between these two components during the reaction process. This confinement in turn results in an approximate capacity decay of 5% over the course of 10 cycles. Next **Table 4. 5** presents the influence of one-dimensional carbon materials on the hydrogen storage characteristics of MgH₂ for direct comparison.

Table 4. 5 How One-dimensional carbon materials effect on the hydrogen storage properties of MgH_2 . [21]

Composites	Preparation Method	Hydrogen Absorption	Hydrogen Desorption
MgH_2 +CNTs	Wet impregnation & ultra-high pressure	Absorb 5.7wt.% H_2 at 275°C under 8MPa in 10min	Release 5.7wt.% H_2 at 300°C in 60min
MgH_2 +10wt.% Ni@CNFs	Ball milling	Absorb 6.0wt.% H_2 at 300°C under 3MPa	Release 5.79wt.% H_2 at 280°C
MgH_2 +5wt.% SWNTs	Ball milling	Absorb 6wt.% H_2 at 200°C under 2MPa in 10min	Release 6wt.% H_2 at 350°C in 5min
MgH_2 +5wt.% SWNTs+ NbF_5	Ball milling	Absorb 5.2wt.% H_2 at 100°C under 2MPa in 10min	Release ~4wt.% H_2 at 300°C in 15min
$Mg(H_xF_{1-x})_2$	Ball milling	–	Release 4.6wt.% H_2 at 434
MgH_2 +5wt.% MWCNTs	Ball milling	Absorb 6.5wt.% H_2 at 300°C under 2MPa in 3min	Release ~1.2wt.% H_2 at 300°C in 20min
MgH_2 +0.5wt.% CNTs+4.5wt.% V-based catalyst	Ball milling	Absorb 6.50wt.% H_2 at 200°C under 2MPa in 1min	Release all H_2 at 300°C in 10min
MgH_2 +5wt.% ZrO_2 +5wt.% CNTs	Ball milling	Absorb ~6.73wt.% H_2 at 150°C under 3MPa in 2min;	Release 6.24wt.% H_2 at 300°C in 15min
MgH_2 +NiFe@CNTs	Ball milling	Absorb 4.06wt.% H_2 at 100°C under 3.25wt.% at 75°C	Initial desorption temperature 225°C
MgH_2 +10wt.% TiFe+5wt.% CNTs	Ball milling	Start to absorb H_2 at room temperature under 3MPa	Release ~6.5wt.% H_2 at 300°C
MgH_2 +CNTs+Ni	Ball milling	Absorb 7.20wt.% H_2 at 200°C in 30min	Release 7.29wt.% H_2 at 250°C in 60min
MgH_2 +5wt.% CNFs	Ball milling	–	Release ~5wt.% H_2 at 300°C in 20min
MgH_2 +helical CNFs	Ball milling	Absorb ~5.5wt.% H_2 at 300°C under 20MPa in 15min	Release H_2 at 300°C
MgH_2 +10wt.% CFs	Ball milling	Absorb 5.3wt.% H_2 at 300°C under 1MPa	Release 5.8wt.% H_2 at 330°C
MgH_2 +Ni@pCNFs	Wet impregnation & hydrogenation	Absorb 4.3wt.% H_2 at 250°C under 3MPa in 10min	Release 4.1wt.% H_2 at 300°C

4.17.11 Two-dimensional carbon materials

Two-dimensional layered porous carbons, characterized by meticulously engineered structures and regulated electronic properties, possess significant promise for applications in the energy sector. By augmenting the interlayer spacing in these carbon materials, one can achieve an expanded surface area that reveals a wealth of surface atoms and electroactive sites. Consequently, this enhancement leads to superior electrical conductivity and surface area, rendering them exceptionally suitable for a range of energy-related applications [21].

4.17.11.1 Graphene

Graphene is a notable two-dimensional carbon material, distinguished by its honeycomb structure formed by carbon atoms in a thin film configuration. This distinctive arrangement provides ample space for the distribution of Mg/MgH₂ and various catalysts.

In their research, Wang et al. [100] successfully synthesized composites featuring MgH₂ particles with sizes as small as 3 nm through a ball milling process that included LiH and MgCl₂ in conjunction with graphene. The MgH₂-10 wt.% graphene composite exhibited exceptional performance, capable of releasing about 5.1 wt.% H₂ at 325 °C within a span of 20 minutes and absorbing 5 wt.% H₂ in just 10 minutes at 250 °C under a hydrogen atmosphere of 2 MPa. Jain et al. reported that the incorporation of graphene results in a reduction of the dehydrogenation activation energy of MgH₂ by around 34 kJ·mol⁻¹, alongside a decrease in the initial dehydrogenation temperature by approximately 128 °C. Graphene materials exhibit significant potential for enhancing the cycling performance of MgH₂. Recent investigations have further highlighted the catalytic effects of graphene and graphene-based materials in improving the hydrogen storage capabilities of MgH₂. Verma et al. developed a composite of graphene-templated TiH₂ (TiH₂@Gr) and observed that it lowered the onset desorption temperature of MgH₂ to 204 °C, which is 31 °C and 36 °C lower than the temperatures recorded for MgH₂-Ti@Gr and MgH₂-TiO₂@Gr, respectively. Additionally, Verma et al. [125] investigated the catalytic effects of graphene and vanadium disulfide on MgH₂, finding that the onset desorption temperature for MgH₂-VS₂ was 289 °C, which is 11 °C lower than that of MgH₂-Gr. Shukla et al. [126] reported the enhanced catalytic performance of graphene-templated CuO (CuO@Gr), noting that the onset desorption temperature for MgH₂-(CuO)@Gr was reduced to 229 °C. This improvement in hydrogen storage performance was attributed to the synergistic interaction between CuO nanoparticles and graphene. Furthermore, Kesarwani et al. [127] succeeded in synthesizing graphene quantum dots (GQDs) characterized by a high density of disordered defects through a microwave-assisted green synthesis method, utilizing them as catalysts to improve the hydrogen storage capabilities of MgH₂. Their findings indicated that incorporating 7 wt.% GQDs decreased the dehydrogenation enthalpy of MgH₂ from 74 kJ·mol⁻¹ to 58 kJ·mol⁻¹. Remarkably, after undergoing 25 hydrogenation/dehydrogenation cycles, the 7% GQDs@MgH₂ composite retained a reversible hydrogen storage capacity of 4.91 wt.%, with a minimal capacity loss of less than 5% compared to the initial rehydrogenation capacity of 5.15 wt.% [21].

The remarkable cyclic stability observed can be largely ascribed to the effects of electron transfer on the intrinsic defects and discrete energy levels of graphene quantum dots (GQDs), which significantly enhance charge transfer during the hydrogen absorption and desorption processes of magnesium hydride (MgH₂). In their study, Zhang et al. [100] utilized first-principles calculations to investigate the influence of graphene on the performance of MgH₂ dehydrogenation. Their

findings indicated that the excellent dispersion properties of graphene inhibited the aggregation of MgH_2 particles, although it slightly diminished the reduction in particle size that typically results from ball milling. The incorporation of graphene led to a decrease in the dehydrogenation activation energy to $94.01 \text{ kJ}\cdot\text{mol}^{-1}$, representing a reduction of $75.51 \text{ kJ}\cdot\text{mol}^{-1}$ compared to pure MgH_2 . Additionally, Fu et al. [101] developed nitrogen-doped graphene-supported titanium monoxide (TiO@N-C) as a highly effective catalytic precursor to enhance the hydrogen storage capabilities of MgH_2 . High-resolution transmission electron microscopy (HRTEM) analysis indicated that the interplanar distance of 0.326 nm corresponded to the (110) crystal plane of TiO_2 , while the darker regions exhibited diffraction spots corresponding to the (110) crystal plane of TiO . Energy-dispersive spectroscopy (EDS) mapping confirmed the uniform distribution of titanium, oxygen, nitrogen, and carbon within the TiO@N-C composite. The presence of these uniformly distributed catalytic particles, along with the nitrogen-doped graphene support, significantly improved the hydrogen storage performance of MgH_2 . Furthermore, Shaw et al. elucidated that graphite primarily functions to disperse particles, promote grain refinement, and prevent agglomeration. Their research on a highly reactive composite system involving LiBH_4 and MgH_2 ball-milled aerosols supports this conclusion [102].

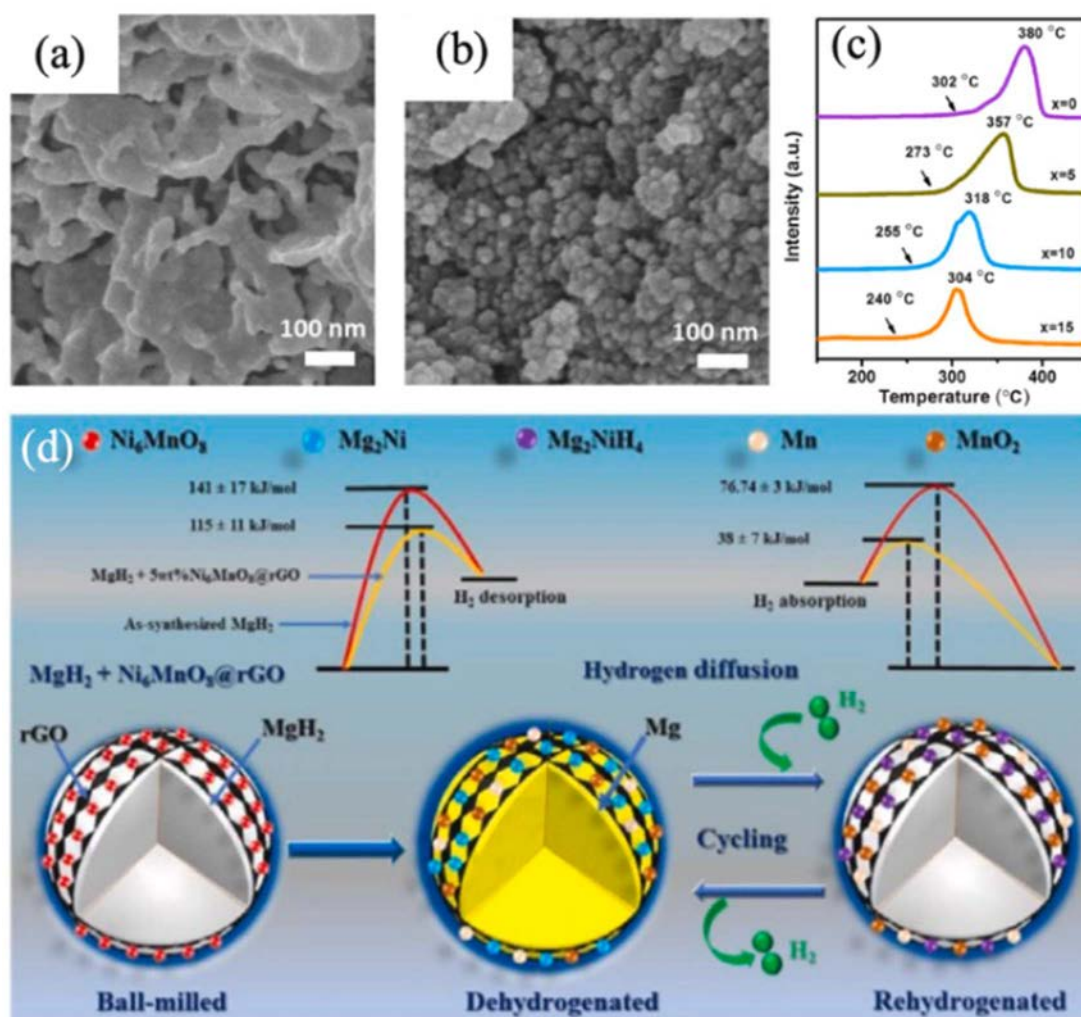


Figure 4. 15 SEM images of (a) MgH_2 and (b) MgH_2 -10 wt.% graphene, (c) Thermally programmed dehydrogenation curves of composites; (d) Schematic diagram of the catalytic mechanism of

Notably, graphite does not engage directly in the reaction and retains a stable amorphous form both prior to and following the reaction. Yu et al. [47] aimed to encapsulate MgH₂ within a nanostructure utilizing graphene via wet impregnation. The resulting composite exhibited minimal sensitivity to temperature fluctuations during hydrogen release. Interestingly, under a hydrogen atmosphere of 3 MPa, the hydrogen absorption rate at 280 °C exceeded that at 320 °C, with approximately 4.5 wt.% H₂ absorbed within 80 minutes. These results underscore a significant challenge: increasing the loading amount during the wet impregnation process would result in a gradual increase in the size of MgH₂ particles on the graphene surface. Conversely, decreasing the loading amount would adversely affect the hydrogen storage capacity of the composite material. Thus, while graphene-nanoconfined MgH₂ presents new opportunities for nanoscale hydrogen storage solutions, achieving an optimal balance between hydrogen storage capacity and kinetic performance remains a considerable challenge. Recent studies have also emphasized the role of graphene in preventing the agglomeration of catalytic nanoparticles and MgH₂ during hydrogen cycling. The enhanced cyclic stability has been attributed to the anchoring effect of graphene, which offers structural support and dispersion for the nanoparticles [102], [105].

Reduced graphene oxide (rGO) represents a highly promising material for enhancing the hydrogen storage capabilities of MgH₂. In a study conducted by Li et al. [106], MgH₂ was ball milled with 10 wt.% rGO that was loaded with Ni nanoparticles. This process led to a significant decrease in the initial hydrogen release temperature of MgH₂, lowering it from 251 °C to 190 °C. The resulting composite could release 6.1 wt.% H₂ within 15 minutes at 300 °C and absorb 5 wt.% H₂ at 100 °C under a 3 MPa hydrogen atmosphere. Similarly, Zhu et al. [112] utilized NiCu-loaded rGO to create a MgH₂-5 wt.%NiCu/rGO composite, which demonstrated an initial dehydrogenation temperature of 185 °C, markedly lower than the 300 °C required for pure ball-milled MgH₂. Upon heating to 300 °C, this composite released 5.5 wt.% H₂ within 1000 seconds and absorbed 5 wt.% H₂ at 200 °C under a 3 MPa hydrogen atmosphere in under 2 minutes. However, it is noteworthy that approximately 0.5 wt.% H₂ could not be released during the cycling process at 300 °C. Guemou et al. [114] reported a significant reduction in the activation energies for dehydrogenation ($115 \pm 11 \text{ kJ}\cdot\text{mol}^{-1}$) and hydrogenation ($38 \pm 7 \text{ kJ}\cdot\text{mol}^{-1}$) of MgH₂ by employing 5 wt.% Ni₆MnO₈-anchored rGO, in comparison to pure MgH₂. This innovation facilitated the release of 5.4 wt.% H₂ within 10 minutes at 275 °C, and after complete hydrogen desorption, the composite was able to absorb 3.3 wt.% H₂ within 30 minutes at 100 °C under a 3 MPa hydrogen atmosphere. Importantly, the composite exhibited exceptional stability, with no significant capacity loss observed over 20 cycles at 300 °C. The catalytic roles of in-situ produced Mg₂Ni/Mg₂NiH₄, Mn, and MnO₂, along with the stabilizing effect of reduced graphene oxide (rGO), promote an even dispersion and uniform particle size of the nanoparticles. This plays a crucial role in improving the hydrogen

storage performance of the composite material [42].

4.17.11.2 Mxene

Recently, the development of two-dimensional materials known as Mxenes has attracted substantial interest in catalysis, largely because of their remarkable properties. Mxenes are defined as a group of materials that are primarily composed of layered transition metal carbides and nitrides. Mxenes that contain stacked layers of transition metal carbides have shown notable potential as catalysts or additives in magnesium-based hydrogen storage technologies [21].

The SEM image depicts the morphological characteristics of Mxene, which exhibits a block-like structure. This configuration is marked by the systematic layering of its components, like that of multilayer graphene. A straightforward blending technique [128] demonstrated that the incorporation of 5 wt.% Ti_2C material resulted in a significant reduction of 37 °C in the initial hydrogen desorption temperature of MgH_2 . Zou et al. [129] effectively utilized a self-assembly method to create highly dispersed MgH_2 nanoparticles on the surface of 3D $\text{Ti}_3\text{C}_2\text{Tx}$ (Ti-MX), as shown in **Figure 4. 16**. This composite underwent decomposition at 140 °C, releasing 3.0 wt.% H_2 within a span of 150 minutes. Remarkably, after 60 cycles at 200 °C, the reversible hydrogen capacity achieved an impressive 4.0 wt.% H_2 . It was evident that the nanoconfinement of Ti-MX, along with the in-situ generation of the TiH_2 catalyst, significantly contributed to the enhancement of hydrogen storage capabilities. The schematic representation of this mechanism is illustrated in **Figure 4. 16** [21], [129].

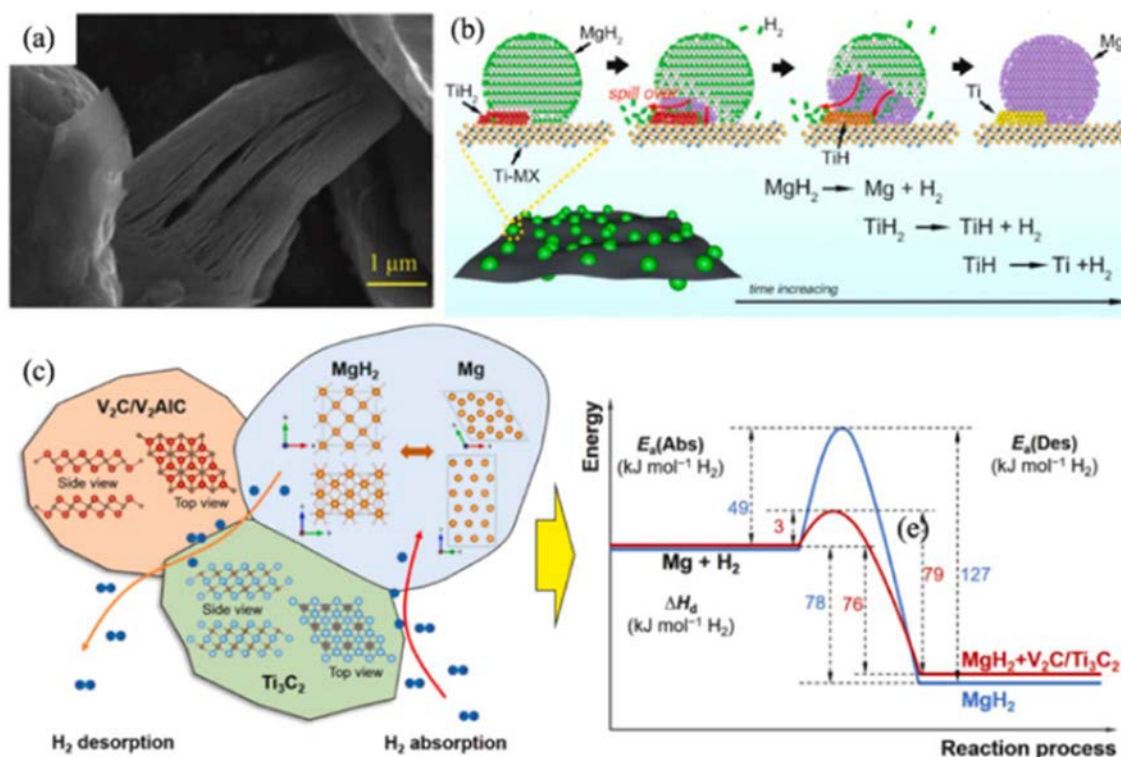


Figure 4. 16 (a) SEM image of Ti_2C [128]; (b) Schematic of mechanism for the fast dehydrogenation [129](c) Schematic of $\text{MgH}_2 + \text{V}_2\text{C}/\text{Ti}_3\text{C}_2$ reaction mechanisms and energy barriers[21].

In their study on $\text{Ti}_3\text{C}_2\text{Tx}$, Gao et al. [130] highlighted the significance of in-situ generated titanium species (Ti-C , Ti^{2+} , Ti^{3+} , TiO_2 , and Ti_0) during the hydrogen storage process. These species played a crucial role in facilitating charge transfer and enhancing the recombination of hydrogen atoms into molecular hydrogen on the surface of the material, leading to a marked improvement in dehydrogenation kinetics. Liu et al. [131] reported an enhancement in the hydrogen storage capabilities of MgH_2 through the incorporation of V_2C and Ti_3C_2 . The initial dehydrogenation temperature for MgH_2 -10 wt.% $\text{V}_2\text{C}/\text{Ti}_3\text{C}_2$ composite was recorded at 180 °C, enabling the release of 5.1 wt.% H_2 within 60 minutes at 225 °C, and achieving a release of 5.8 wt.% H_2 in just 2 minutes at 300 °C. Following complete dehydrogenation, the composite demonstrated the ability to absorb 5.1 wt.% H_2 in 20 seconds at a low temperature of 40 °C under a hydrogen pressure of 6 MPa. Additionally, the composite exhibited a reversible capacity of 6.3 wt.% over 10 cycles at 300 °C. The proposed hydrogen storage mechanism for the MgH_2 - V_2C - Ti_3C_2 system suggest that during the absorption phase, hydrogen atoms or molecules preferentially migrate through the interfaces of $\text{MgH}_2/\text{V}_2\text{C}/\text{Ti}_3\text{C}_2$ and are ultimately absorbed at the $\text{Mg}/\text{Ti}_3\text{C}_2$ interface. The inclusion of V_2C and Ti_3C_2 significantly lowers the activation energy barriers associated with hydrogen absorption and desorption in the MgH_2 - V_2C - Ti_3C_2 composite. The activation energy for absorption decreases from 49 kJ/mol to 3 kJ/mol, while the desorption of activation energy is reduced from 127 kJ/mol to 79 kJ/mol. Furthermore, the enthalpy change for the dehydrogenation reaction is diminished from 78 kJ/mol to 76 kJ/mol, indicating enhanced thermodynamic destabilization.

Zhu et al. [132] reported that the MgH_2 -5 wt.% $\text{Nb}_4\text{C}_3\text{Tx}$ composite had a significantly reduced initial hydrogen release temperature from 296.5 °C to 150.6 °C. It desorbed 6 wt.% H_2 within only 15 min when heated up to 250 °C, and after full hydrogen desorption, the composite was able to absorb 3.50 wt.% H_2 even at 50 °C under 3 MPa hydrogen atmosphere. The unique layered structure of Mxene and in situ formation of NbH_x in this paper significantly reduced the activation energy for the hydrogen release and uptake of MgH_2 -5 wt.% $\text{Nb}_4\text{C}_3\text{Tx}$ composite from 153.8 kJ/mol and 82.1 kJ·mol⁻¹ to 81.2 kJ·mol⁻¹ and 27.8 kJ·mol⁻¹, respectively. It is worth noting that Wang et al. [133] reported the capacity of MgH_2 -9wt.% NbTiC composite, which could release 5.8 wt.% H_2 within 30 min upon heating to 250 °C and absorb 5.3 wt.% H_2 under 5 MPa hydrogen atmosphere when heated to 150 °C and even at such a low temperature as 50 °C, up to 4.0 wt.% H_2 within 15 min. Li et al. [134] intelligently adopted non-metal elements co-doping into Nb_2CTx and then achieved a breakthrough in preparing composite materials, namely the MgH_2 +5% N/S- Nb_2CTx composite. From experiment tests, 225 °C released the composite up to ~4.78 wt. % H_2 in 30 minutes; on the contrary, composite sorbs around 4.00 wt% of H_2 under conditions at 30 °C/30 bar for 80 minutes. The dehydrogenation apparent activation energy of the composite decreases to 70.00 kJ·mol⁻¹ H_2 , much lower than that of MgH_2 + Nb_2CTx (99.44

$\text{kJ}\cdot\text{mol}^{-1} \text{H}_2$) and MgH_2 ($133.19 \text{ kJ}\cdot\text{mol}^{-1} \text{H}_2$) systems. This improvement is mainly due to the stable layered structure of the N/S–Nb₂CT_x catalyst, which supplies plenty of nucleation sites for MgH_2/Mg , while the in situ formed species like Nb and NbO₂ contribute to the weakening of the strength of Mg–H bonds. Moreover, the co-doping of N and S effectively enhances the ability of multivalent Nb to promote electron transfer between Mg^{2+} and H^- , further accelerating the hydrogen diffusion process. The effects of two-dimensional carbon materials on the hydrogen storage properties of MgH_2 have been listed in the next **Table 4. 6** for direct comparisons.

Table 4. 6 *Two-dimensional carbon materials on the hydrogen storage properties of MgH_2 [21]*

Composites	Preparation Method	Hydrogen Absorption	Hydrogen Desorption
$\text{MgH}_2 + 10\text{wt.}\%$ $2\text{V}_2\text{C}/\text{Ti}_3\text{C}_2$	Ball milling	Absorb 5.1 wt.% H_2 at 40°C under 6MPa in 20s	Release 5.1 wt.% H_2 at 225°C in 60min; Initial dehydrogenation temperature 180°C
$\text{MgH}_2 + \text{Graphene}$	Ball milling	Absorb 5 wt.% H_2 at 250°C under 2MPa in 10min	Release ~5.1 wt.% H_2 at 325°C in 20min
$\text{MgH}_2 + \text{Graphene}$	Ball milling	–	Initial dehydrogenation temperature 282°C
$\text{MgH}_2 + \text{Graphene}$	Wet impregnation	Absorb ~4.5 wt.% H_2 at 280°C under 3 MPa in 80min	–
$\text{MgH}_2 + 10\text{wt.}\%$ $\text{rGO} + \text{Ni}$	Ball milling	Absorb 5 wt.% H_2 at 100°C under 3MPa	Release 6.1 wt.% H_2 at 300°C in 15min; Initial dehydrogenation temperature 190°C
$\text{MgH}_2 + 5\text{wt.}\%$ NiCu/ rGO	Ball milling	Absorb 5 wt.% H_2 at 200°C under 3 MPa in <2min	Release 5.5 wt.% H_2 at 300°C in 1000s; Initial dehydrogenation temperature 185°C
$\text{MgH}_2 + 5\text{wt.}\%$ $\text{Ni}_6\text{MnO}_8/\text{rGO}$	Ball milling	Absorb 3.3 wt.% H_2 at 100°C under 3MPa in 30min	Release 5.4 wt.% H_2 at 275°C in 10min;
$\text{MgH}_2 + 5\text{wt.}\%$ Ti_2C	Simple blending	–	Initial dehydrogenation temperature 423°C
$\text{MgH}_2 + 3\text{D Ti}_3\text{C}_2\text{Tx}$	Self-assembly	Absorb 4.0 wt.% H_2 at 200°C	Release 3.0 wt.% H_2 at 140°C in 150min; Initial dehydrogenation temperature 140°C
$\text{MgH}_2 + 5\text{wt.}\%$ $\text{Nb}_4\text{C}_3\text{Tx}$	Ball milling	Absorb 3.50 wt.% H_2 at 50°C under 3MPa	Release 6 wt.% H_2 at 250°C in 15min; Initial dehydrogenation temperature 150.6°C
$\text{MgH}_2 + 9\text{wt.}\%$ NbTiC	Ball milling	Absorb 5.3 wt.% H_2 at 150°C under 5MPa	Release 5.8 wt.% H_2 at 250°C in 30min
$\text{MgH}_2 + 5\%$ N/S– Nb_2CT_x	Ball milling	Absorb 4.00 wt.% of H_2 at 30°C and 30bar 80min	Release 4.78 wt.% H_2 at 225°C in 30

4.17.12 Three-dimensional carbon materials

Three-dimensional carbon materials, including carbon nanospheres and activated carbon, exhibit a significant surface area and a porous architecture, coupled with commendable chemical stability. These characteristics effectively minimize the ion diffusion distance, thereby facilitating outstanding kinetic performance. As a result, they have become focal points in various research domains, such as gas adsorption, separation techniques, and energy storage solutions. The highly interconnected and adjustable porous structures of these materials, along with their robust mechanical stability, render them particularly appealing for these applications [115].

4.17.12.1 Carbon nanosphere (CNS)

Carbon nanospheres, recognized for their robust adsorption properties, elevated catalytic performance, and efficient dispersion, have made considerable contributions to the advancement of magnesium-based hydrogen storage materials.

Pan et al. [111] prepared a composite catalyst that includes ultrafine nickel nanoparticles evenly dispersed on porous hollow carbon nanospheres. Optimal performance is achieved for 90% Ni content in the composite along with 5 wt.% of this material and MgH_2 . $\text{MgH}_2/\text{Ni}_{90}@\text{PHCNSs}$ shows a decrease in both the initial and peak hydrogen release temperatures to 190 °C and 242 °C, respectively. Under heated conditions at 250 °C for 30 min, it was able to release 6.2 wt.% H_2 . After complete hydrogen desorption, this composite was able to reabsorb 6.2 wt.% H_2 in 250 s upon heating at 150 °C under a 5 MPa hydrogen atmosphere. It was observed that after 50 cycles of dehydrogenation at 350 °C in vacuum and subsequent rehydrogenation at 250 °C under the hydrogen atmosphere of 5 MPa, its hydrogen storage capacity remained constant as high as 6.4 wt.%. This is said to be improved due to highly dispersed nickel nanoparticles reacting with MgH_2 forming the nanoscale $\text{Mg}_2\text{Ni}/\text{Mg}_2\text{NiH}_4$ system, and this acts catalytically for the reaction. In addition, carbon nanobubbles (CNBs) act as a spacer, increasing dispersion and impeding the agglomeration and growth of Mg/MgH_2 . More recently, Han et al. [135] synthesized nitrogen-doped carbon spheres coated by nickel nanoparticles ($\text{Ni}@\text{CNS}$) through a chemical reduction method. After that, the composite material $\text{MgH}_2\text{--Ni}@\text{CNS}$ was synthesized through hydrogen combustion and high-energy ball milling. It was observed that the $\text{MgH}_2\text{--Ni}@\text{CNS}$ composite reached a hydrogen storage capacity of 5.7 wt.% in 8 min at 350 °C, while desorbing 4.3 wt.% at the same temperature. This catalyst demonstrated remarkably excellent performance at temperatures as low as 100 °C, being able to uptake as high as 4.2 wt.% hydrogen within 60 min compared with 0.9 wt.% absorbed by the as-ball-milled MgH_2 .

No significant capacity degradation of the composite was observed after 10 cycles at 350 °C under 3 MPa hydrogen pressure. In-situ formed Mg_2NiH_4 , responsible for easy

decomposition of MgH_2 , had been considered as the reason for the improvement of hydrogen sorption performance of the composite. Besides, the carbon incorporation could effectively prevent the agglomeration and growth of the Mg/MgH_2 particles during cycling. Shaz et al. [136] prepared a composite of $\text{MgH}_2\text{--Fe--CNS}$ by ball-milling MgH_2 with carbon nanospheres doped with iron nanoparticles. The resulting composite desorbed 5.6 wt.% H_2 at 226 °C and absorbed an equal amount of H_2 in 55 seconds at 300 °C under a hydrogen atmosphere of 2 MPa. It is worth noting that the apparent activation energy of hydrogen release from the composite was determined to be as low as $84.9 \text{ kJ}\cdot\text{mol}^{-1}$, far lower than that of pure MgH_2 at $130 \text{ kJ}\cdot\text{mol}^{-1}$. Accordingly, Fe^{3+} was reduced to Fe^{2+} , and a multivalent environment was constructed in this process. Furthermore, $\alpha\text{-Fe}$ doping in Mg/MgH_2 caused a shift of the Fermi level, therefore enhancing vacancy-assisted hydrogen diffusion. Besides, Fe_3C confirmed that the Fe nanoparticles have good adherence to the carbon atoms of HCS. In fact, both together improved kinetic properties of hydrogen storage material. Moreover, the agglomeration of Fe nanoparticles and the hindering role of Mg grain growth were important roles played by the HCS. In recent work, Cheng et al. [47] prepared bimetallic PdNi nanoparticles supported on mesoporous carbon CMK3 ($\text{Pd}_{30}\text{Ni}_{70}/\text{CMK3}$) to improve the low temperature de/rehydrogenation performance of MgH_2 . By XRD analysis, it was observed that, under the adopted conditions, the primary cause of thermodynamical destabilization was the formation of the Mg_6Pd intermediate phase, due to the reaction of Pd with MgH_2 , while the Ni nanoparticles played a mainly catalytic role. Li et al. [137] prepared a novel flowerlike carbon-coated CoFe alloy nanoparticle catalyst synthesized from MOFs with the aim to optimize the hydrogenation and dehydrogenation properties of MgH_2 . HRTEM studies showed that CoFe alloy nanoparticles in the size range between 10 and 20 nm were wrapped by the carbon layers produced by the decomposition of MOFs. The interplanar distance of 0.117 nm was associated with the (110) planes of CoFe alloy, and the spacing of 0.335 nm was assigned to a characteristic plane (002) of carbon. The synergistic action of CoFe alloy nanoparticles and carbon coating brings a marked improvement in the hydrogen storage performance of MgH_2 [21].

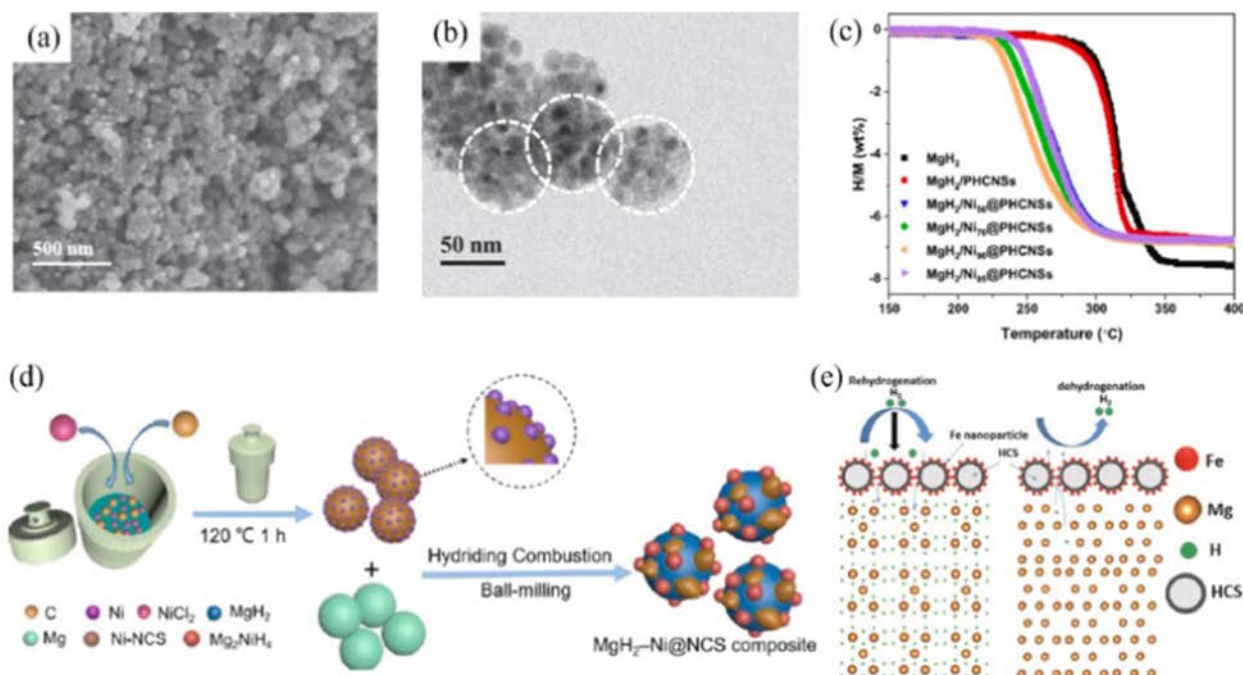


Figure 4. 17 $\text{Ni}_{90}\text{@PHCNSs}$ composites (a) SEM (b)TEM, (c) TPD curves of the $\text{MgH}_2/\text{Ni}_x\text{@PHCNSs}$; (d) preparation schematic diagram of $\text{MgH}_2\text{-Ni@CNS}$ composite ; (e) Diagrammatic illustration of sorption cycle in Fe loaded CNS catalyzed MgH_2 [21].

4.17.12.2 Activated Carbon

The activated carbon materials are also usually called amorphous carbon materials; they possess a huge specific surface area and adjustable pore structures and thus are particularly useful in catalysis and the confinement of nanostructures. In their work, Ma et al. [138] prepared a nano-Ni catalyst supported on mesoporous carbon CMK-3 (Ni@C) by carbonization of dimethylglyoxime dinickel chelate. TEM characterizations indicated that the nickel nanoparticles with an average size of 7.5 nm were well dispersed and partly enveloped by carbon layers. The onset dehydrogenation temperature of MgH_2 was lowered by 113°C through the addition of Ni@C . Moreover, 6.0 wt.% H_2 could be released within 500 s at 300°C , and the dehydrogenation activation energy was reduced by 79.9 kJ/mol. Excellent absorption and desorption cycling ability of the $\text{MgH}_2\text{-5%Ni@C}$ composite was determined at 275°C . From XRD and TEM measurements, it is identified that a portion of nickel transforms into $\text{Mg}_2\text{NiH}_4/\text{Mg}_2\text{Ni}$ phases after the cycling process [21].

The improved catalytic effect of Ni@C should be mainly ascribed to the strong interaction among the well-distributed ultra-fine Ni nanoparticles and MgH_2 . In Zhang et al. 's study [139], the identification of an amorphous carbon-coated Mg-based hydrogen storage material was designed by mechano-chemical technique wherein reactive ball milling of MgH_2 with fluorene was used. Amorphous carbon layer coats the surface of Mg/MgH_2 , thus effectively inhibiting the agglomeration and growth, but also providing considerable channels for H_2 diffusion.

Consequently, the dehydrogenation activation energy was lowered from $161.2 \text{ kJ}\cdot\text{mol}^{-1}$ to $87.1 \text{ kJ}\cdot\text{mol}^{-1}$, and the onset hydrogen release temperature decreased from 378°C to 284°C . Upon heating to 350°C , the material could release 5.31 H_2 within 10 min. More interestingly, it could absorb $4.93 \text{ wt.}\%$ H_2 within 1 min at 200°C under a hydrogen atmosphere of 3 MPa. Zhu et al. [98] supported Ni nanoparticles on CMK-3 and then ball milled the obtained mixture with MgH_2 . This co-catalytic approach, with both Ni and CMK-3, reduced the dehydrogenation activation energy to $43.4 \pm 2.0 \text{ kJ}\cdot\text{mol}^{-1}$. As a result, the MgH_2 -10 wt.% Ni/CMK-3 composite showed hydrogen release starting at 160°C , completing at 295°C , with a total of $6.6 \text{ wt.}\%$ H_2 . It could also absorb $5.7 \text{ wt.}\%$ H_2 within 40 minutes at 150°C under a hydrogen atmosphere of 3 MPa. Lan et al. [140] skillfully integrated hydrothermal techniques with high-temperature carbonization to produce a titanium-nitrogen co-doped carbon nanocatalyst, $\text{TiN}@C$, which was later used in the MgH_2 hydrogen storage system. The investigation shows that the MgH_2 + $\text{TiN}@C$ composite can release $6.0 \text{ wt.}\%$ of hydrogen within 15 min at 300°C , and the initial dehydrogenation temperature is lowered to 226°C . After dehydrogenation, the sample can reabsorb $5.80 \text{ wt.}\%$ of hydrogen at 200°C , and the apparent activation energy for hydrogen absorption decreases from $77.6 \text{ kJ}\cdot\text{mol}^{-1}$ to $44.9 \text{ kJ}\cdot\text{mol}^{-1}$, thus exhibiting outstanding kinetic performance. Mechanistic research suggests that the addition of titanium components is essential in enhancing the kinetics of the composite, while the activated carbon part, though it does not have a significant catalytic effect, plays a vital role in ensuring the uniform distribution of the catalyst within the MgH_2 matrix. Recent studies have shed light on the high-resolution structural analysis of carbon materials incorporated with MgH_2 . Pukazhselvan et al. [141] prepared a TiO_2/AC composite and studied its effect on the hydrogen storage properties of MgH_2 . The TEM analysis revealed that TiO_2 nanoparticles with a size of 20–30 nm was well dispersed on the surface of activated carbon; some of the particles were partially embedded in the MgH_2 matrix. The introduction of these embedded TiO_2 nanoparticles enhanced the formation of trapping centers and diffusion pathways for hydrogen, thereby enhancing hydrogen storage capacity [21].

Activated carbon materials have excellent advantages in terms of pore volume and pore size, which are especially appropriate for generating nanostructure confinement in MgH_2 . One study by Jong et al. [115] used heating magnesium into the liquid phase followed by letting it get incorporated into porous carbon to increase the Nano structuring confinement of magnesium. The findings have shown the importance of modifying the surface features of porous carbon to decrease surface oxygen functional groups and prevent pore blockage resulting from the formation of MgO . Such modification, which could probably be achieved by nitrogen doping, is essential for facilitating a more homogeneous and increased incorporation of magnesium into the porous carbon structure. Moreover, to improve the filling density and fully exploit the smaller pores, a rational pore distribution is necessary, which allows the formation

of Mg nanocrystals of smaller size. Jongh et al. [110] used a similar method, molten MgH_2 impregnation, to incorporate Ni nanoparticles on activated carbon.

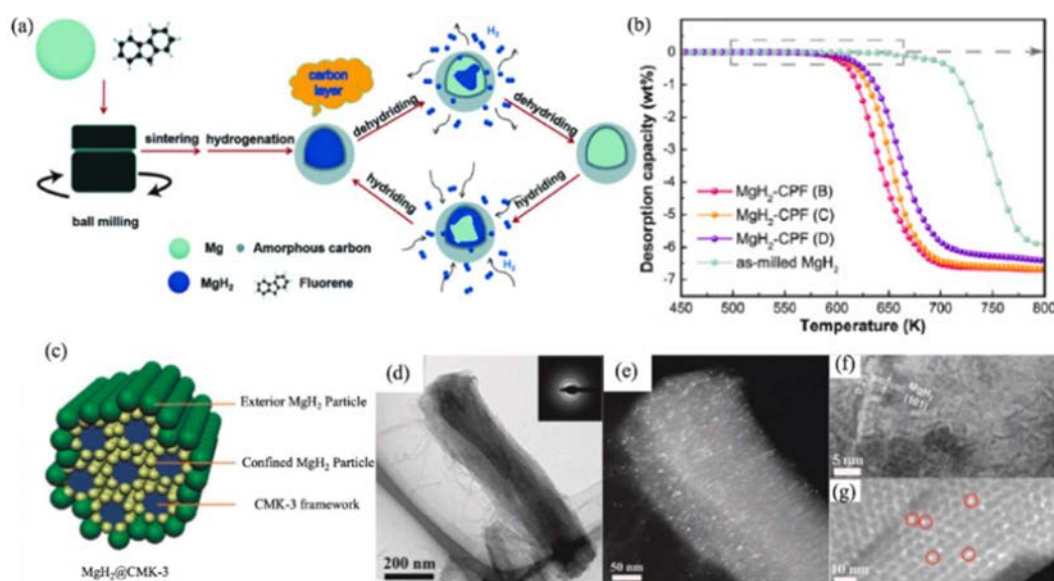


Figure 4. 18 MgH_2 -AC composite (a) Schematic of the synthesis and hydrogenation/dehydrogenation processes and (b) TPD curves [97]; $0.6\text{MgH}_2\text{@CMK-3}$ (c) Schematic model, (d) Bright-field image of $0.6\text{MgH}_2\text{@CMK-3}$ with an inset of a selected area electron diffraction (SAED)[21]

The grain sizes of $\text{Mg}_2\text{Ni/Mg@AC}$ composites were found to be in the range of 10–30 nm. While the kinetic performance of these materials has not been extensively studied, it is posited that the formation of Mg_2NiH_4 during hydrogen absorption and desorption processes contributes positively to the overall hydrogenation characteristics of the composite. Additionally, activated carbon (AC) materials have proven particularly effective in enhancing the hydrogen storage capabilities of MgH_2 . Research conducted by Paskevicius et al. [113] demonstrated that the confinement of MgH_2 nanoparticles within AC led to improved hydrogen desorption performance and enhanced cycling stability. The porous nature of AC facilitated a uniform distribution of MgH_2 nanoparticles, thereby improving the thermal conductivity of the composite.

Beside the molten impregnation method, the wet impregnation process using AC materials is also applied to create nanostructure confinement. Jensen et al. put carbon aerogel (CA) in dibutylmagnesium, then hydrogenated at 170 °C and 5–5.5 MPa hydrogen for 24 h to produce $\text{MgH}_2\text{@CA}$. Experimental data showed that the rate of loading MgH_2 in the carbon aerogel was 15–17 wt.%, and 12 wt.% was reversible hydrogen storage system for 10 cycles. This method was employed by Nielsen et al. [142] to synthesize nanostructured MgH_2 and the authors reported that it was able to liberate all H_2 when dynamically heated at a heating rate of 2 °C/min to 367 °C and initial hydrogen release temperature of 175 °C. It was found that the pore size distribution of the support material significantly affects the hydrogen desorption kinetics of nanoconfined MgH_2 , with smaller pores facilitating faster desorption rates. Buckley et al. [111] confined MgH_2 nanoparticles, measuring 2 nm, within carbon aerogel, which effectively altered the thermodynamics of the composite, initiating hydrogen release at 100 °C. However, it is noteworthy that the kinetics remained relatively slow, and

the complete loading of MgH_2 within the CA pores was not achieved. Yao et al. [143] successfully incorporated 37.5 wt.% of 1–2 nm-sized MgH_2 nanoparticles into CMK-3 through the wet impregnation method [21].

The TEM image confirms that the impregnation and hydrogenation processes did not alter the morphology or structure of CMK-3. The observed lattice fringes with an interplanar spacing of 0.25 nm is ascribed to the (101) plane of MgH_2 . Therefore, these results confirm that the MgH_2 nanoparticles are fully encapsulated in the CMK-3 porous structure. It has been found that the electron conduction between the carbon matrix and MgH_2 changes the thermodynamic characteristics of the system and, therefore, weakens the Mg–H bonds and induces hydrogen liberation at 50 °C. Nevertheless, the kinetic characteristics of this composite are not optimal and there is a need for further improvements for the target applications. The influence of three-dimensional carbon materials on the hydrogen storage characteristics of MgH_2 is summarized in next **Table 4. 7** [21].

Table 4. 7 Three-dimensional carbon materials on the hydrogen storage properties of MgH₂. [21]

Composites	Preparation Method	Hydrogen Absorption	Hydrogen Desorption
MgH ₂ +Ni ₉₀ @PHCNSs	Ball milling	Absorb 6.2wt.% H ₂ at 150°C under 5MPa in 250s	Release 6.2wt.% H ₂ at 250°C in 30min; Initial dehydrogenation temperature 190°C
MgH ₂ +Ni@CNS	Hydrogen combustion & ball milling	Absorb 5.7wt.% H ₂ at 350°C in 8min	Release 4.3wt.% H ₂ at 350°C
MgH ₂ +Fe-CNS	Ball milling	Absorb 5.6wt.% H ₂ at 300°C under 2MPa in 55s	Release 5.6wt.% H ₂ at 226°C
MgH ₂ +Pd ₃₀ Ni ₇₀ /CMK-3	Ball milling	Absorb 4wt.% H ₂ at 70°C under 3MPa	Release 1.3wt.% H ₂ at 100°C
MgH ₂ +Amorphous carbon	Reactive ball milling	Absorb 4.93wt.% H ₂ at 200°C under 3MPa in 1 min	Release 5.31wt.% H ₂ at 350°C in 10min; Initial dehydrogenation temperature 284°C
MgH ₂ +10wt.% Ni/CMK-3	Ball milling	Absorb 5.7wt.% H ₂ at 150°C under 3MPa in 40min	Release 6.6wt.% H ₂ from 160°C to 295°C
MgH ₂ +10% TiN@C	Ball milling	absorb 5.80wt.% H ₂ at 200°C undet 6Mpa	Release 6.0wt.% at 300°C in 15min, Initial dehydrogenation temperature 226°C.
MgH ₂ +AC+Ni	Molten impregnation	Presence of Mg ₂ NiH ₄ during absorption	Presence of Mg ₂ NiH ₄ during desorption
MgH ₂ +CA	Wet impregnation & hydrogenation	–	–
MgH ₂ +CA	Wet impregnation & hydrogenation	–	Release all H ₂ upon heating to 367°C at 2°C/min; Initial dehydrogenation temperature reduced to 175°C
MgH ₂ +CA	Wet impregnation & hydrogenation	–	H ₂ release starts at 100°C
MgH ₂ +37.5wt.% CMK-3	Wet impregnation	–	H ₂ release starts at 50°C

CHAPTER 5

Conclusions

The high demands in energy consumption, coupled with the depletion of oil and gas reserves, has underscored the need for hydrogen-based energy systems. The advantages of unconventional hydrogen storage methods have been highlighted through a comparative analysis of various hydrogen storage technologies. While hydrogen energy systems offer operational efficiency and flexibility, large-scale hydrogen storage and production remain significant challenges to their commercialization and widespread adoption. Thus, a hydrate-based hydrogen storage approach has emerged as a promising alternative for hydrogen storage. This study examines current challenges, recent technological advancements, functional benefits, limitations, and the current capacity for hydrogen storage. A detailed discussion of the thermodynamics and kinetics of hydrate formation has revealed the importance of achieving hydrate stability under moderate conditions, promoting hydrate growth, reducing induction times, and enhancing hydrogen absorption. The fundamental mechanism of hydrogen storage involves the entrapment of hydrogen molecules within hydrate cages, which remain stable under high-pressure and low-temperature conditions. Furthermore, a comprehensive analysis of the thermodynamics of hydrogen-bearing systems at varying promoter concentrations, temperatures, and pressures has been conducted to find out the ideal operating conditions of hydrate-based hydrogen storage. Determining the optimum promoter concentration for hydrogen storage under less severe stability conditions remains one of the most crucial challenges to hydrate-based hydrogen storage commercialization.

This thesis focused on the storage of hydrogen and specifically on various materials that are used for this purpose. In summary, the future of carbon-based materials for Mg-based solid-state hydrogen storage appears promising, with various research directions and strategies offering potential advancements. By focusing on rational design, synergistic effects, advanced characterization and modeling, scalability and cost-effectiveness, and integration with other technologies, researchers can unlock the full potential of carbon-modified MgH_2 systems and contribute to the development of efficient, safe, and sustainable hydrogen storage solutions for a clean energy future.

The cost of hydrogen is projected to decrease to the desired range of \$1-2 per kilogram, a significant reduction from the current price of \$4-7 per kilogram. Hydrogen is distinguished by its exceptional energy-to-weight ratio, which ranges from 120 to 142 MJ/kg, making it one of the most efficient among conventional fuels. The steam methane reforming (SMR) process represents about 48% of the global hydrogen production market, achieving an efficiency of 70-85% and the lowest production costs. Meanwhile, solid oxide fuel cell (SOFC) technology, which is used for

hydrogen conversion and storage, achieves an efficiency of around 70%, although it remains in the demonstration phase. Furthermore, the metal hydride storage system is noted for its lower cost of \$125 per cubic meter in terms of specific volumetric pricing, while ammonia storage offers the most economical energy cost at \$13.3 per GJ among various storage solutions.

The widespread adoption of hydrogen as a fuel in the transportation sector and as a feedstock in the chemical industry remains under consideration. To satisfy this anticipated demand, an entire infrastructure of hydrogen from production through distribution is required. Policies and legislation are integrated by different countries to include hydrogen as a fuel source in the transport and energy industries for achieving net-zero emissions within ten years; therefore, research and development in this area is required. Advancing technologies around hydrogen production, storage, distribution, and transmission are imperative and must be funded by the government.

More research must be conducted to make hydrogen more flexible and available worldwide for various purposes replacing conventional fuels. Key areas of research include, but are not limited to, the efficient and cost-effective conversion of solar energy into hydrogen, innovations in nanoscale catalytic technologies, the development of novel hydrogen storage materials, the creation of low-cost and durable cathodes for low-temperature fuel cells, and a comprehensive review of hydrogen safety protocols.

Although hydrate-based hydrogen storage has been extensively studied and is recognized as a promising future technology, its full commercialization remains unrealized. Continued research and development are required to address existing challenges and bring this technology to practical application.

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