

**ENABLING
PROGRESS
TOWARDS
A GREEN
HYDROGEN
ECONOMY**

**进程加速：
迈向绿氢经济**

CAS



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Introduction

The quest for alternative energy sources has continued for many decades, but today, fossil fuels still account for more than 80% of current global energy consumption.¹ The need to find new energy sources is primarily driven by the imperative requirement to limit or even eliminate carbon emissions in order to mitigate the mounting crisis that is posed by climate change and the fact that natural energy resources are ultimately limited.² The move to tackle this threat facing the planet will require alternative energy sources with safe and reliable means of conversion, storage and usage.² One major proposed option is hydrogen and its use in fuel cells to convert energy into electricity.

The integration of renewable hydrogen production, storage, and utilization into the global energy system is known as the *green hydrogen economy* (GHE).³ Hydrogen is a clean and renewable energy source and has the potential to act as a superior energy carrier; it has a much

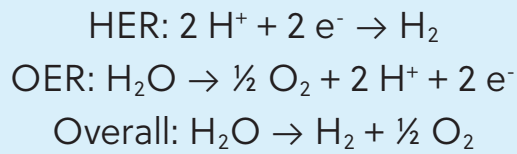
greater energy density (142kJg^{-1}) when compared with fossil fuels ($10\text{-}50\text{kJg}^{-1}$) alongside the absence of carbon emissions.^{4,5} However, the primary mode of producing hydrogen is not currently sustainable; 96% is derived from fossil fuels (natural gas, oil, and coal) which is hardly a suitable route for sustainable energy.⁶ Most (>95%) hydrogen is produced for non-energetic purposes such as ammonia production, which is critical in the synthesis of fertilizers and consequently for food production.⁷ One of the major challenges is that hydrogen has a low ambient temperature density making it hard to store. To make the GHE a reality, safe and efficient technologies of H_2 storage which improve the energy density of hydrogen must be developed.⁸ The availability of renewable technologies for cheaply generating and storing hydrogen to be used on a global scale in sufficient quantities for critical applications such as electricity generation (e.g., for fuel cells) and propulsion is therefore critical.



Methods for hydrogen production, storage, and utilization

Production by water electrolysis

Water electrolysis is critical in efforts for renewable hydrogen production; it proceeds via oxidation of H_2O at the electrolyzer anode to generate O_2 and reduction of hydrogen cations at the cathode to produce H_2 . The two reactions use substantial amounts of electricity and are known as the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER), respectively.⁹



The hydrogen liberated from this electrolysis can be stored and then oxidized to produce energy and water. The above chemical processes can operate in various types of electrolyzer configurations. The main industrial types are the alkaline electrolyzers, but other types include polymer electrolyte membrane (PEM) electrolyzers and solid oxide electrolyzers (SOEs) (Figure 1).¹⁰ The principal challenges of electrolyzers include minimizing internal resistances, optimization of the membrane-electrode assembly, and selection of separator material; these challenges all play a part in the efficiency of the device and are the focus of ongoing research.⁸ Additionally, materials challenges also drive the research in each electrolyzer category, although it is proven that alkaline electrolyzers are a mature and globally commercialized technology.

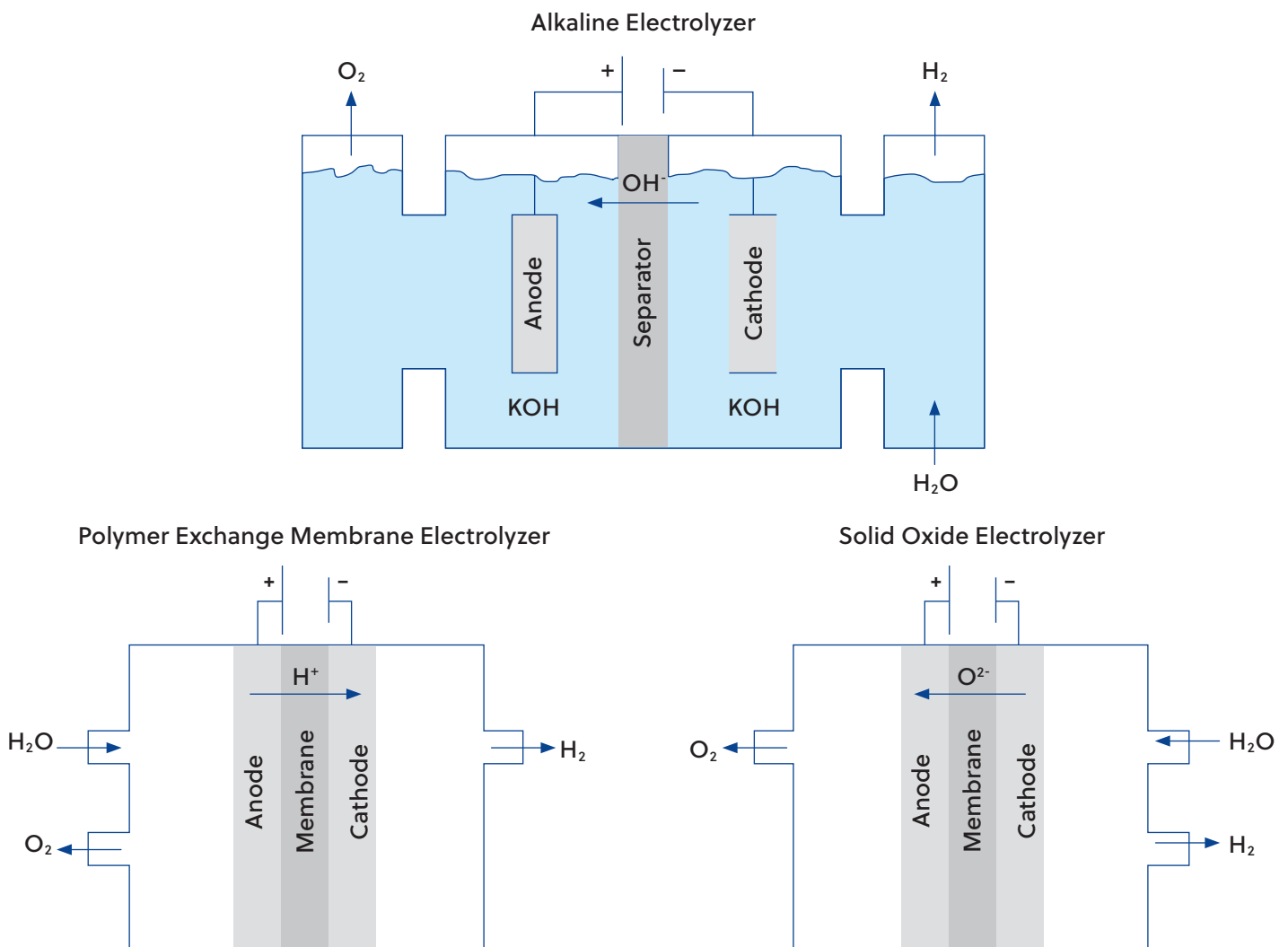


Figure 1. Electrolyzer configurations of interest for application

Hydrogen produced by water electrolysis is only as green as the electricity used in its generation and should, as far as possible, use sustainable sources such as solar and wind. An analysis of the sustainability of hydrogen production technologies found hydrogen production using fossil fuels to be the most environmentally damaging and solar energy to be the least, however, solar and wind had the highest cost.¹¹ The technology that decreases the amount of electricity needed to split water contributes to the overall greenness of the process. This is emphasized by performing electrolysis at high temperatures (e.g., SOEs working at $\sim 1000^\circ\text{C}$) which can decrease the energy for electrolysis by 40%. Better still, other approaches such as direct solar photocatalytic water splitting can reduce or even eliminate the need to apply an electrochemical potential. Photocatalysts and electrocatalysts are currently under development for conventional electrolysis and are key aspects of green hydrogen production.

Hydrogen storage

Hydrogen, although an efficient fuel, is challenging to store compared to other energy sources and greater use will require the development of advanced storage methods capable of safely containing high energy densities.⁶ Storage currently involves either physical-based or chemical-based approaches.

The current top three physical-based storage systems are:

- **Compressed hydrogen**, which is stored in tanks that can be quickly charged and discharged. Hydrogen volume is high, and these are compressed into pressurized tanks which keep the 350-700 bar pressure, and are made of carbon fiber composite materials with a metal liner (aluminum, steel) or polymer liner (polyethylene).¹²⁻¹⁴

- **Liquified hydrogen**, which reduces the volume further and has been used to fuel rockets for many years. This storage is technically complex and costly, requiring high energy, cooling (to near absolute zero), insulation, and strict safety procedures during transfer to eliminate explosion risks^{12,15}
- **Cryo-compressed hydrogen** uses a compression and cooling process in cryogenic tanks. This requires 15.2 kWh/kg to reach a volumetric density of 70.8 kg/m³. A 2-mm stainless steel liner is required for storage pressures up to 700 bar.¹⁶

Compressed and liquified hydrogen storage technologies are yet not sufficiently secure for transport applications, so the development of chemical/material alternatives is of interest (**Figure 2**).

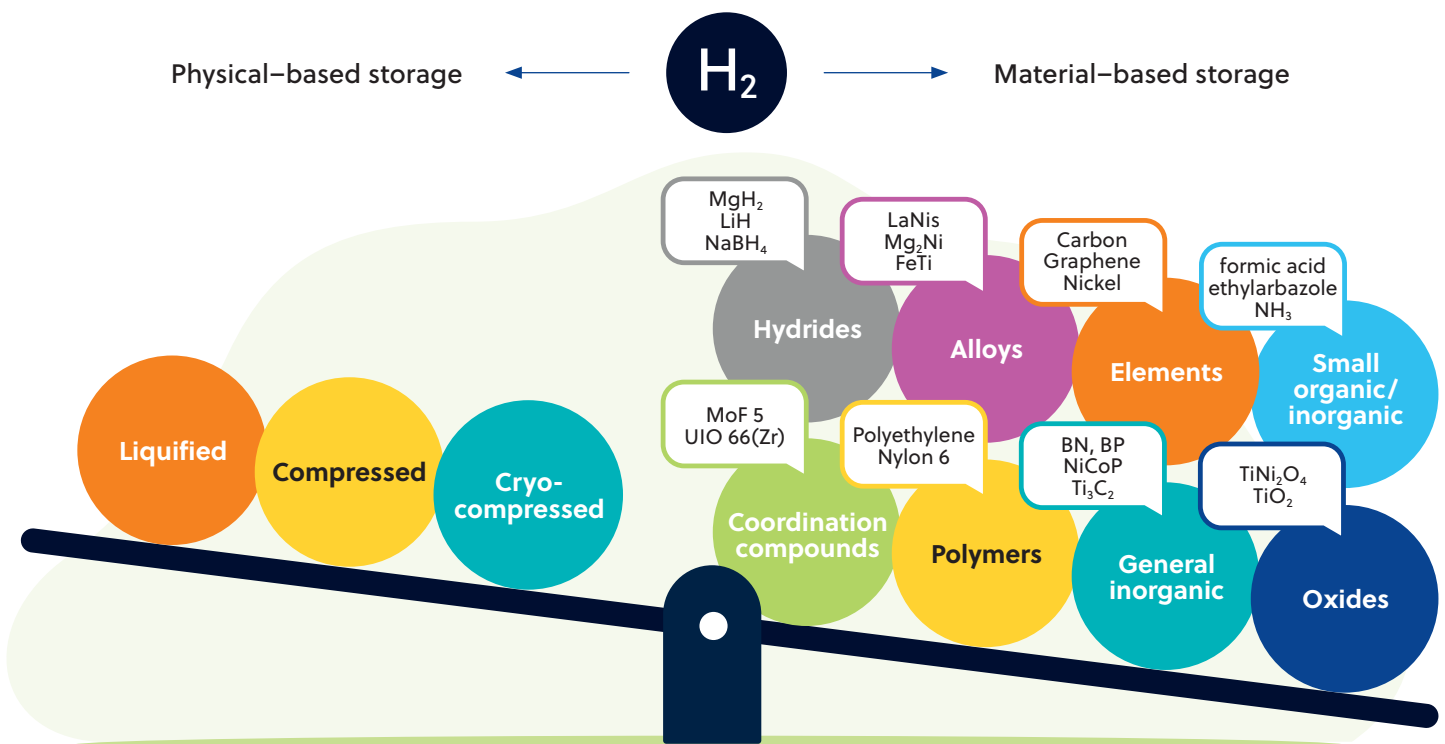


Figure 2. Physical vs. material-based hydrogen storage



Hydrogen storage materials can be divided into two categories based on the relative strength of the material interaction with hydrogen. One of these uses **physisorption**, which is a reversible process with low interaction energy. For physisorbed hydrogen storage materials, H₂ molecules are adsorbed via a weak van der Waals interaction on the surface of the pores; the physisorption process is reversible since the interaction energy is incredibly low. The mechanism for which hydrogen is stored through physisorption in carbon sorbents is proportional to their specific surface area.^{17,18} Advantages of physisorption in sorbents include lower storage pressure without a significant reduction in capacity, and higher storage temperatures (reducing the cost for insulation and energy consumption for cooling). The main drawback is low binding energies

Utilization and commercialization

Fuel cells are electrochemical devices that convert chemical energy into electrical energy and have a diverse range of transport, residential, commercial, military, and even toy applications.²¹ Their advantages include being efficient and clean when compared with combustion engines, being compatible with renewable sources and energy carriers like hydrogen, and having a quiet operation. Fuel cells are similar to batteries but with the difference that fuel can be continuously fed in, enabling an indefinite power supply.²² It should be noted; however, that fuel cells have issues with durability, which can restrict their usefulness and cost-effectiveness in use.²³

for H₂, which can be overcome using cryogenic temperatures.¹² Promising physisorption materials that have the potential for hydrogen storage are carbonaceous sorbents such as activated carbon, carbon nanotubes, graphite, graphene, and metal organic frameworks.¹⁸

The other category of materials uses **chemisorption** in which hydrogen is chemically bonded to the storage medium. This is mostly a non-reversible process due to the relatively high activation energy of the adsorption and desorption process. Examples of chemisorbent materials include metal hydrides, hydrogen storage alloys, and liquid organic hydrogen carriers (formic acid, N-alkylcarbazoles). In use, these require dehydrogenation catalysts (transition metal nanoparticles).^{19,20}

Hydrogen fuel cells use a reverse of water electrolysis. A typical fuel cell has a semi-permeable membrane between a porous cathode and anode.²⁴ At the anode, a catalyst oxidizes hydrogen, producing hydrogen cations and electrons. The hydrogen cations pass through the electrolyte/membrane to the cathode. The electrons, however, pass through an electrical circuit which produces the electric current.²² At the cathode, molecular oxygen combines with the hydrogen protons and electrons to form water (**Figure 3**).

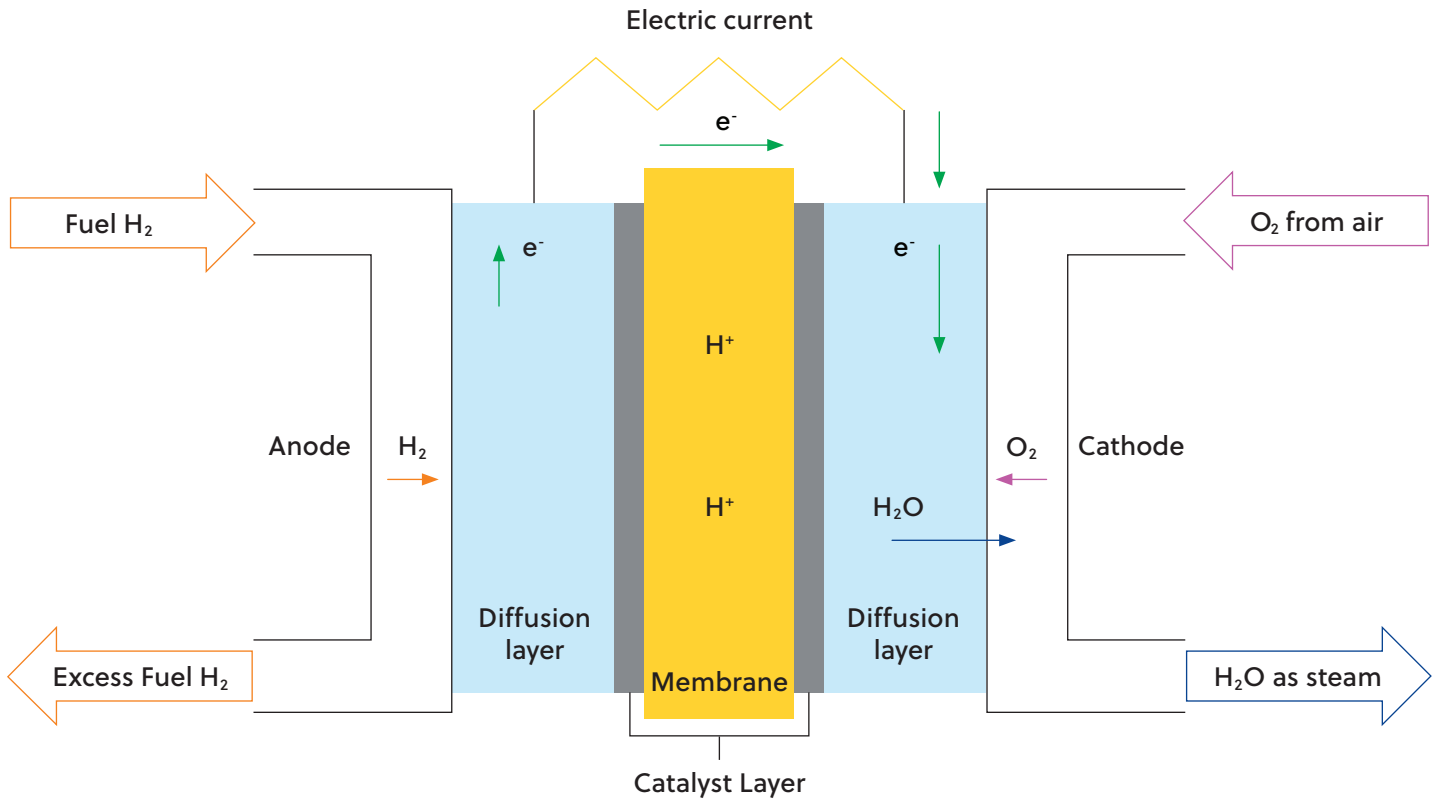


Figure 3. General structure and operation of a hydrogen fuel cell

There are several different types of fuel cells, some of which have been used for many years for a variety of different purposes.

Alkaline fuel cells (AFC) were the first type widely used in the U.S. space program to produce electrical energy and water on spacecraft (e.g., in the Apollo missions and the Space Shuttle) and on vehicles such as forklifts and as stationary power sources.^{25,26} These cells can operate below 100°C, and the electrolyte is a concentrated alkaline solution or an anion exchange membrane. Advantages include using a wide range of electrocatalysts (usually nickel, silver, and platinum). Disadvantages include high sensitivity to contaminants especially poisoning by CO₂. It requires pure hydrogen and oxygen to be used instead of air, but an alkaline membrane can eliminate this requirement.^{21,25,26}

Proton exchange membrane fuel cells (PEMFC) use an acidic membrane (a solid hydrated polymer) that conducts hydrogen cations through its structure when saturated with water. Most commercial PEMFC cells use Nafion, a perfluorosulfonic acid ionomer membrane (Dupont).²⁷ This membrane has a low weight compared with liquids making it suitable for electric vehicles and portable power applications such as the Gemini manned space vehicles.²⁷ Disadvantages are that it must be

hydrated to conduct protons; the membrane must be kept at around 80°C and requires very pure hydrogen with minimal or no CO, but this is mostly resolved using hydrogen produced via water electrolysis.^{21,27,28}

Phosphoric acid fuel cells (PAFC) use phosphoric acid (H₃PO₄) in a silicon carbide electrolyte and operate at higher temperatures, reducing the sensitivity to carbon monoxide poisoning. These can be mostly used in stationary power applications, using waste heat for space heating and hot water. The disadvantages are that it must be heated first to run, needs pure platinum as the catalyst for the cathode, requires platinum-ruthenium alloy as the catalyst for the anode, and is very sensitive to sulfur contamination.^{29,30}

Solid oxide fuel cells (SOFCs) use a ceramic-solid oxide, and a very high operating temperature (600°C -1,000°C) to achieve sufficient ionic conductivity.^{31,32} These cells are mostly used for stationary applications and for the production of electrical and thermal energy known as combined heat and power.^{29,31} Their advantages include no need for a precious-metal catalyst (thus leading to a reduced cost), being sulfur-resistant, and not susceptible to poisoning by carbon monoxide. The disadvantages of these cells include high operating temperature, slow startup, significant thermal shielding, durability issues, and strict material requirements.^{23,30,31}



Global publication trends in GHE technologies

This white paper uses data from the CAS Content Collection™ to analyze academic and patent literature from 2011-2021 on green hydrogen production, hydrogen storage, and hydrogen-based fuel cells. This will enable an understanding of GHE research trends, the general progress of each field, classes of materials, and concepts driving their innovation.

A search of the GHE literature published during 2011-2021 retrieved 107,293 journal articles and 79,193 patents. Most of the publications were from China, Japan, the U.S., the Republic of Korea, and Germany (Figures 4 and 5). The most prolific publisher of journal articles was China, which

also showed the largest growth largely due to the country's drive to achieve carbon neutrality by 2060. The second highest publisher was Japan which also published the most patents throughout the decade (Figure 4). This rate, however, is decreasing despite the country investing heavily in Hydrogen technologies (Figure 5). The third highest publisher was the U.S. which produced more journal articles than patents (Figure 4); interest in GHE there decreased slightly throughout the decade (Figure 5). Nevertheless, clean hydrogen is crucial to the U.S. Department of Energy's strategy of achieving a 100% clean electrical grid by 2035 and net-zero carbon emissions by 2050.³³

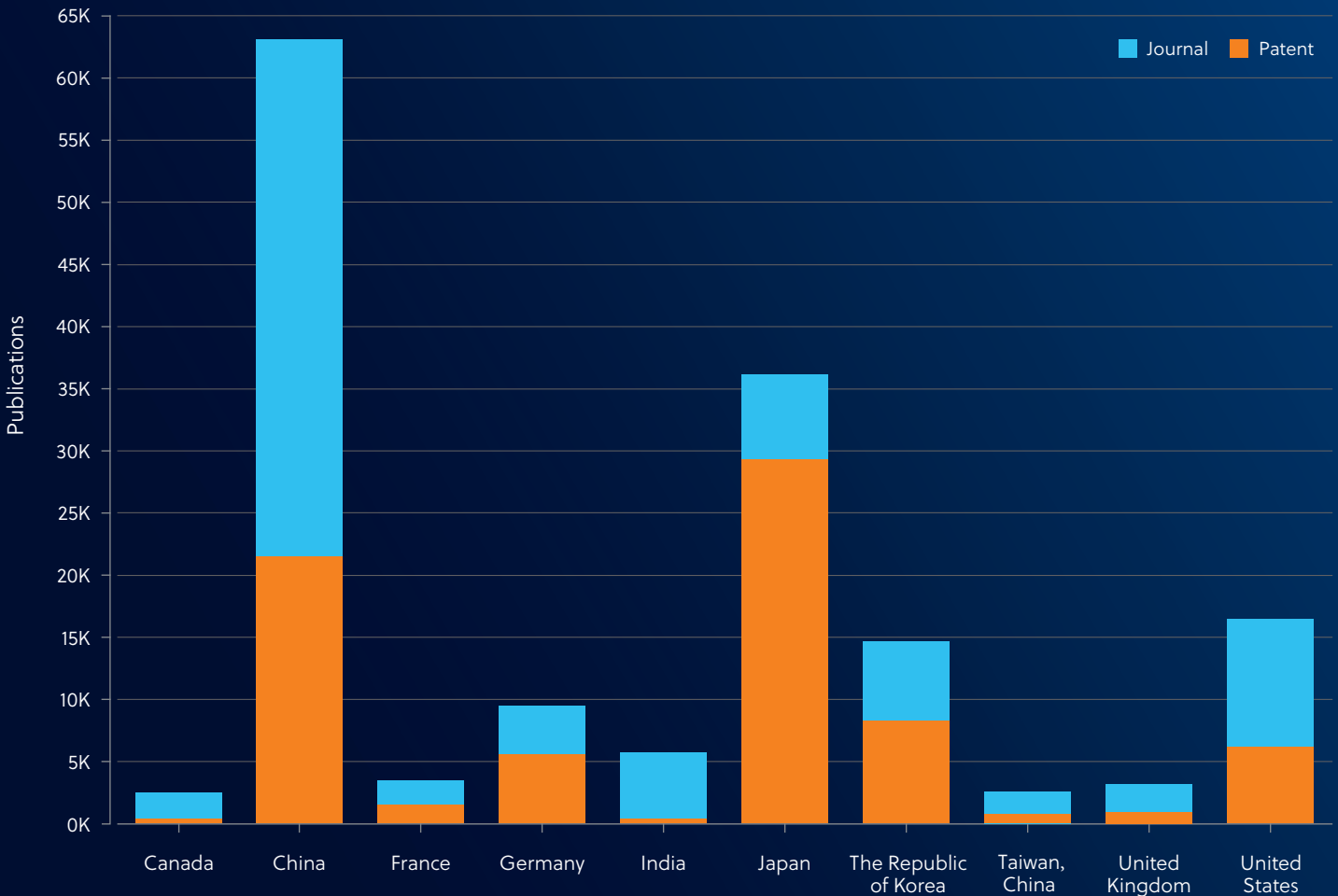


Figure 4. Journal and patent publications on GHE by top organization countries/regions

The timeline in **Figure 5** also demonstrates that the Republic of Korea had an increase in journal publications in the latter half of the decade, with patents staying linear; Germany began to show more interest later in the decade, especially in patents. India has also shown a steady increase in journal publications throughout the decade.

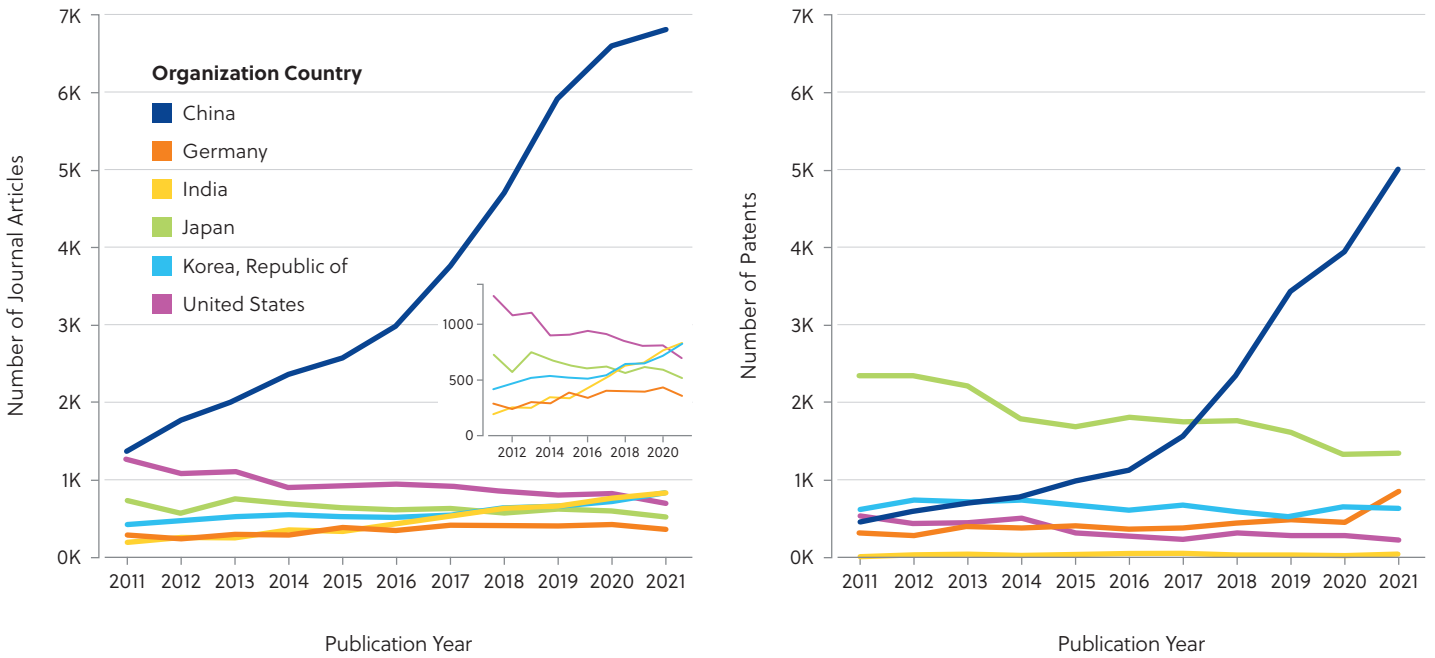


Figure 5. Journal articles and patents over time on GHE for selected countries/regions

The number of annual publications in each GHE research area is given in **Figure 6**. Between 2011 and 2021, there was an over five-fold increase in the publication of both journal articles and patents in green hydrogen production, but this volume appears to be leveling off.



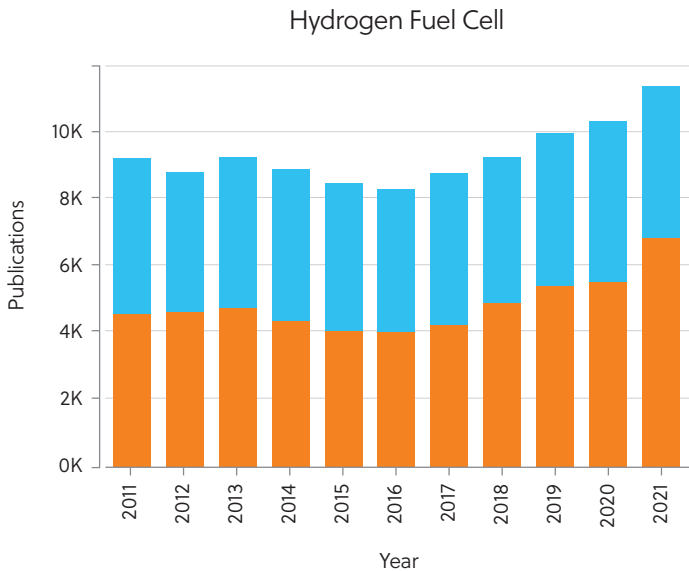
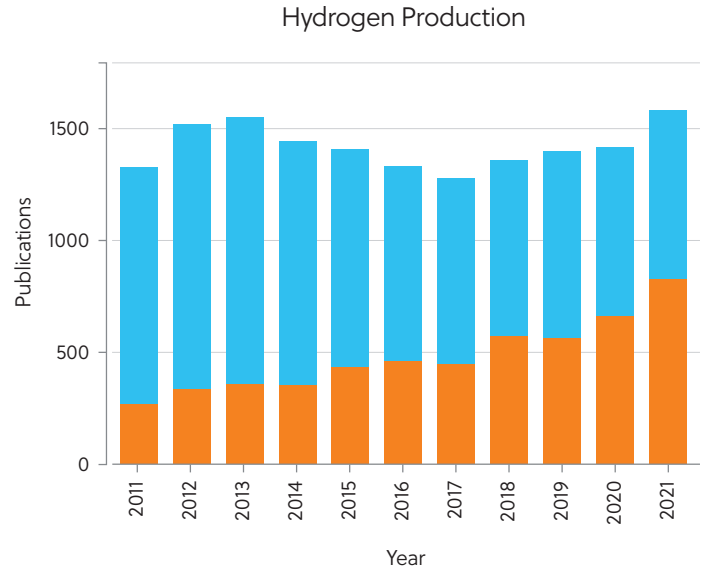
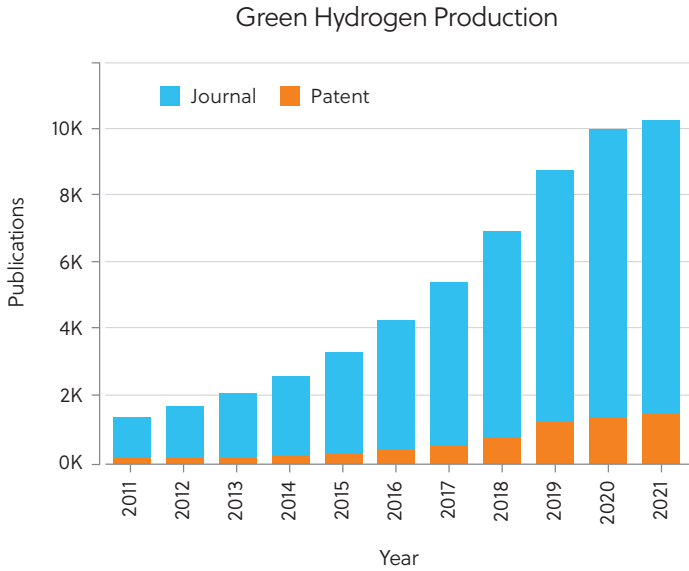


Figure 6. Publication trends in each area of green hydrogen economy research

In contrast to green hydrogen production, the number of annual publications on hydrogen storage fluctuated during 2011-2021. There was a surge in publications on hydrogen storage during 2012-13, which coincided with the appearance of the first commercially produced hydrogen fuel cell vehicle (Hyundai ix35 FCEV). This was followed by a decrease in such publications up to 2017, and then by a slight increase in 2018-2019, stabilization in 2020, and a significant increase in 2021. Meanwhile, there was a steady growth in hydrogen storage patents over the entire period with fewer fluctuations which

may indicate interest by automotive and electronics manufacturers in developing new on-board hydrogen storage technologies. The trend in hydrogen fuel cell publications was essentially stable at the beginning of the decade with a slight dip in 2015-2016 immediately followed by an increase. A breakdown of these findings by country shows that the greatest numbers of publications on GHE overall came from China, followed by Japan and the U.S. (**Table 1**), but Japan published the most articles and patents on hydrogen fuel cells.

Table 1. Journal articles and patents on GHE by top-producing countries/regions from 2011-2021

Country/Region	Green Hydrogen Production		Hydrogen Storage		Hydrogen Fuel Cells	
	Journal	Patent	Journal	Patent	Journal	Patent
China	24,528	4,829	4,041	3,190	13,747	14,311
Japan	2,188	405	709	970	4,193	28,134
United States	3,785	356	842	391	6,093	5,492
Korea, Republic of	2,475	218	420	377	3,635	7,707
Germany	1,616	222	326	226	2,087	5,278
India	2,553	75	634	25	2,269	252

Companies in the Japanese automotive industry (Toyota, Honda, Hyundai, and Nissan) are leading the way in hydrogen fuel cell patent publication (**Table 2**). These companies are developing a range of new fuel cell vehicles, including cars, trucks, and buses.³⁴⁻³⁸ Electronics and appliance manufacturing companies,

such as Panasonic and Bosch, were also leading publishers of patents during 2011-2021. Panasonic has recently launched a 5-kW hydrogen fuel cell generator and plans to use this method to power some of its manufacturing facilities in Japan.^{39,40}

Table 2. Top patent assignees on GHE in each research area from 2011-2021 (Multinational companies are combined under individual names)

Assignee	Number of Patents		
	Green Hydrogen Production	Hydrogen Storage	Hydrogen Fuel Cells
Toyota	37	205	6,768
Honda	22	28	2,893
Hyundai	7	41	1,964
Panasonic	21	47	1,651
Nissan	2	11	1,629
Bosch	24	14	1,171



Materials research directions for GHE

Green hydrogen production technologies

Water electrolysis is an energy-intensive process, but this can be reduced using catalysts. The most commonly used catalysts are platinum for hydrogen evolution and RuO₂ for oxygen evolution. An important research focus is to identify alternative catalysts with performances similar to that of these scarce metals or to find catalysts with a reduced metal loading.^{41,42}

Examining substance information in publications provided further insights into GHE research. The number of distinct substances in GHE publications during 2011-

2021 (**Figure 7**) showed a general increase in research on green hydrogen production catalysts. There was also increased interest in general inorganic compounds, organic/inorganic small molecules, polymers, and oxides. The slight dip in publication numbers from 2019 contrasts with overall publication rates seen in (**Figure 6**). These findings suggest that green hydrogen production catalysis appears to be reaching maturity as a research field with commercial potential.

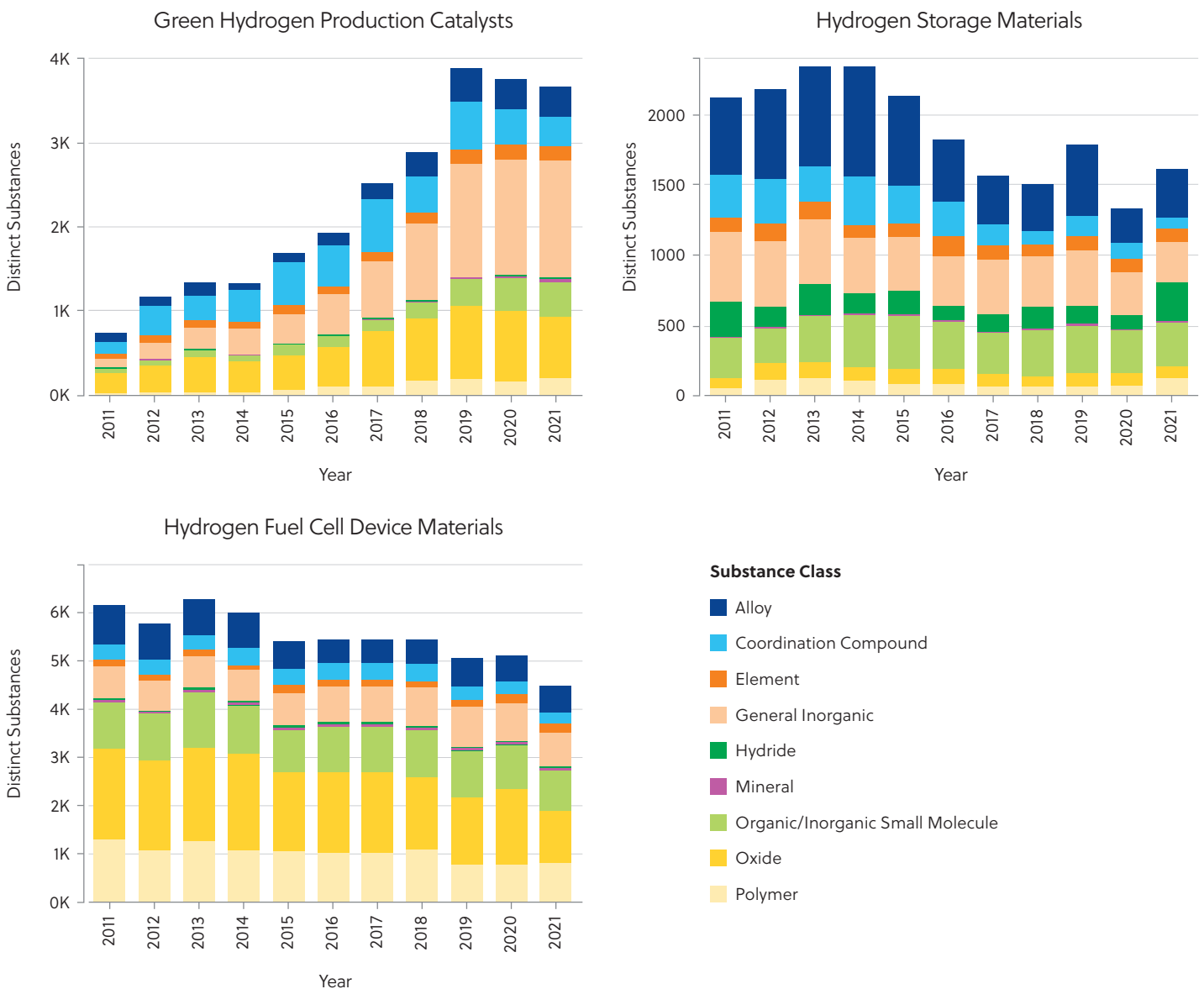


Figure 7. Distinct substances used by year in each area of GHE research from 2011-2021

Looking at relevant substance classes over the decade, there was increased interest in alloys and elements to be used as alternative electrocatalysts to platinum or photocatalysts.⁴³ There was increased interest in coordination compounds in the first half of the decade, which then leveled off. Metal organic framework (MOF)-based and MOF-derived materials saw increased interest as heterogeneous catalysts.⁴⁴ General inorganics and oxides were increasingly applied to green hydrogen production throughout the decade alongside their use as catalyst supports.^{45,46} In addition, polymers began to be studied as components in heterojunction catalysts,⁴⁷ as tunable stand-alone porous photocatalysts (in the case of covalent organic frameworks),⁴⁸ and as precursors to engineered carbonaceous catalyst materials.^{49,50} The top-studied materials from these classes in 2021 are shown in **Table 3** alongside their respective important research focuses.

Control and exploitation of nanoscale morphology is currently a strong focus of research in green hydrogen production catalysts. Key substances identified in the 2011-2021 literature for this application included oxides such as RuO_2 and TiO_2 ,⁵¹⁻⁵⁶ which are frequently used in nanocomposite electrocatalysts. General inorganics included C_3N_4 , which is amenable to vacancy engineering for photocatalysis and MoS_2 which can be used in semiconductor nanosheets for photocatalysis.⁵⁷⁻⁶²

Elements identified for green hydrogen catalyst research included carbon which is used to control morphology and doping level of (photo) electrocatalyst components. Platinum is used in nanostructured or "single-atom" catalysts for decreased loading of the metal in HER. It can also be combined with nickel to create

a foam for in-situ transformations producing active nano-catalyst components and single atom catalysts.⁶³⁻⁶⁹ Coordination compounds used as green hydrogen catalysts included $\text{UiO-66}(\text{NH}_2)$ as a visible light-responsive porous photocatalyst component and ZIF-67 for the production of doped, surface-engineered catalysts; it can also be calcined to produce novel Co-based (photo) electrocatalysts.⁷⁰⁻⁷⁵

Alloys in green hydrogen production catalyst research included an iron-nickel and cobalt-nickel mixture, which can be used with other materials to form nanocomposite electrocatalysts.⁷⁶⁻⁸¹ Finally, polymers that were identified as important in green hydrogen catalyst research were polyaniline and polypyrrole. These are used to create conductive polymers in nanocomposite (photo) electrocatalysts.⁸²⁻⁸⁶

The relative prevalence of the most common nanomaterial types in GHE research found in the 2011-2021 literature is presented in **Table 3**, normalized to the number of publications in each respective research area. For nanotechnology-related concepts in green hydrogen production, the 'nanoparticles' concept was the most common, followed by 'nanosheets' and 'nanocomposites'. Notably, platinum nanoparticles are considered among the top-performing HER electrocatalysts. Nanosheets (2-dimensional materials) have been the subject of much catalyst research in recent years⁸⁷ and can be combined with other materials into nanocomposites with high surface areas that can take advantage of nanoscale effects such as quantum confinement⁸⁸ and surface plasmon resonance,⁸⁹ as well as interfacial effects including the aforementioned semiconductor heterojunctions and Schottky junctions.⁹⁰



Table 3. Top nanotechnology-related concepts in each area of GHE research from 2011-2021

# Publications	Concept	Green Production	Storage	Fuel Cells	Proportion of Publications
14,810	Nanoparticles	●	●	●	0.1465
6,314	Nanosheets	●	●	●	0.1000
4,990	Nanocomposites	●	●	●	0.0500
4,505	Nanostructures	●	●	●	0.016
2,455	Nanorods	●	●	●	0.016
2,285	Nanowires	●	●	●	0.016
1,965	Nanotubes	●	●	●	0.016
1,732	Nanocrystals	●	●	●	0.016
1,731	Nanostructured materials	●	●	●	0.016
1,666	Nano-catalysts	●	●	●	0.016
1,379	Nanofibres	●	●	●	0.016
758	Core-shell nonoparticles	●	●	●	0.016
652	Nanospheres	●	●	●	0.016
608	Nanoporous materials	●	●	●	0.016
584	Nanoclusters	●	●	●	0.016

The relative prevalence of elements in catalysts used for green hydrogen production on a document-level basis is below in **Figure 8**. Overall, an emphasis on carbonaceous materials as well as transition metal oxides and sulfides is apparent. A strong interest was seen in critical metals, including cobalt, nickel, and platinum, with the peak publication volume centered at the expected d⁸ transition metals typical of HER catalysts.

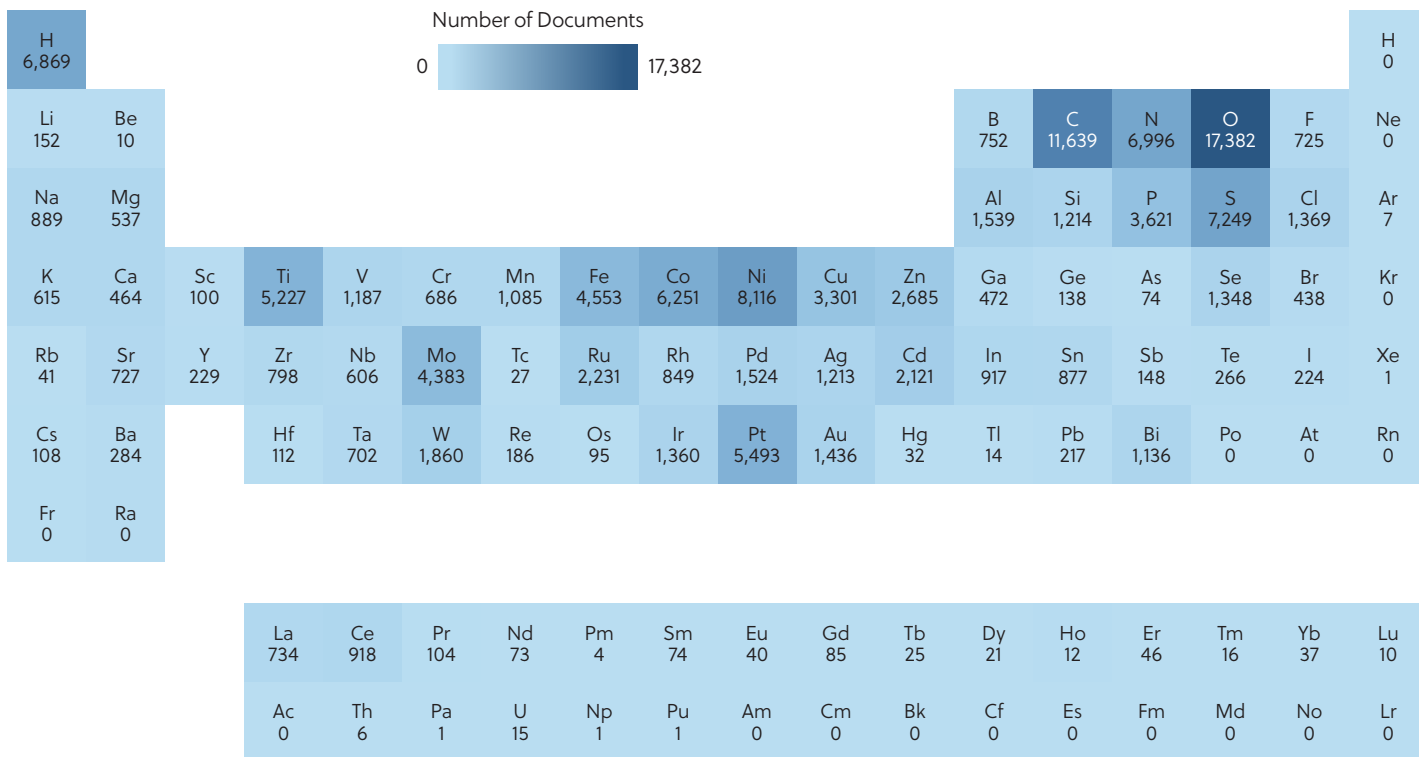


Figure 8. Occurrence of elements in materials used as green hydrogen production catalysts by number of documents from 2011-2021

Hydrogen storage trends

Literature analysis showed that research on hydrogen storage materials (**Figure 7**) declined after peaking in 2013 peak but has increased more recently. Hydrogen storage was mainly associated with alloys, general inorganic, organic/inorganic small molecules, and hydrides which were the focus of research. Publications also continued to feature elements and oxides representing carbonaceous sorbents, dehydrogenation catalysts, and modifiers. The substances in hydrogen storage research are numerous, the most significant of which are outlined in **Table 4**.

Table 4. Key substances in hydrogen storage research

Substance class	Example substances	Description
Alloys	LaNi ₅ , ⁹¹ Mg ₂ Ni, ⁹² FeTi, ⁹³ Stainless Steel ⁹⁴	Intermetallic compounds - reversibly absorb, store, and release hydrogen in large quantities at a given temperature and pressure without compromising their own structure - represent an excellent solution for fuel cell storage
Hydrides	MgH ₂ , ⁹⁵ LiH, ⁹⁶ NaBH ₄ , ⁹⁷ AlH ₃ , ⁹⁸ LiAlH ₄ , ⁹⁹ Mg(BH ₄) ₂ ¹⁰⁰	Prominent hydrogen storage materials function at feasible working temperatures and have a good hydrogen storage capacity. New regeneration method for NaBH ₄ could enable greater use
Elements	Carbon, ^{101,102} Graphene, ¹⁰³ Graphite, ¹⁰⁴ Nickel ¹⁰⁵	Carbonaceous sorbents are promising materials for hydrogen storage due to low densities, good stability, high surface area, and porosity. Research focuses on increasing effective adsorption temperature
Small organics	9-ethylcarbazole, ¹⁰⁶ Methylcyclohexane, ¹⁰⁷ Ammonia, ¹⁰⁸ Ammonia Borane, ¹⁰⁹ Formic Acid ¹¹⁰	Ammonia and formic acid could be used as liquid fuel versions of hydrogen – they are easily prepared and have higher densities which is better for storage and transport. Ammonia borane is a stable solid at room temperature, melts at a temperature of 110 – 114°C, and is a promising chemical hydrogen storage material for use in fuel cells in the automotive industry
Small inorganics	UiO-66(Zr), ¹¹¹ Triaqua[μ-[1,3,5-benzene tricarboxylato(3-kO1:kO'1)]] [μ3-[1,3,5-benzenetricarboxylato(3-kO1:kO3:kO'1)]tricopper ¹¹²	Porous organic polymers, hyper-crosslinked polymers, and polymers with intrinsic microporosity reversibly store and release hydrogen through hydrogen physisorption on their highly porous structures. N-ethylcarbazoles are liquid organic hydrogen storage materials but are hampered by the need for dehydrogenation catalysts
Coordination compounds	Zinc Tris[μ-[1,4 benzenedicarboxylato (2-)-kO1:kO'1]]-m4-oxotetra ¹¹³	Use metal organic frameworks (MOFs), in which hydrogen is physisorbed on the surface of the pores. High storage capacities can be achieved at liquid nitrogen temperature and high pressures. MOFs have been extensively studied as promising hydrogen storage materials
Oxides	MgO ¹¹⁴ Nb ₂ O ₅ ¹¹⁵	Thermochemical storage using a reversible metal oxide redox cycle with hydrogen as a reducing agent and H ₂ O as an oxidizing agent. The best hydrogen storage oxides such as Fe ₃ O ₄ , GeO ₂ , MoO ₂ , SnO ₂ , ZnO, and WO ₃ are supported with Al ₂ O ₃ , TiO ₂ , Cr ₂ O ₃ , MnO, and MgO
Polymers	Polyethylene Glycol, ¹¹⁶ Nylon 6 ¹¹⁷	Porous organic polymers, hyper-crosslinked polymers, and polymers with intrinsic microporosity reversibly store and release hydrogen through physisorption on their highly porous structures
Nanomaterials	Carbon and Boron Nitride Nanotubes, ¹¹⁸ Metal Hydride Nanoparticles, ¹¹⁸ Complex Hydride/Carbon Nanoclusters ¹¹⁸	Nanostructured systems, including carbon and boron nitride nanotubes, metal hydride nanoparticles, complex hydride/carbon nanoclusters, polymer, and metal organic frameworks nanocomposites can store substantial amounts of hydrogen. These have attracted great interest in recent years and are widely used



The overall element distribution in hydrogen storage research (**Figure 9**) shows that carbon is a prevalent element (a major part of carbonaceous sorbents - activated carbon, graphene MOFs) in liquid organic hydrogen carriers and polymers. Other important storage elements are magnesium (with a broad application as a part of metal hydrides, borohydrides, and hydrogen storage alloys [MgH₂, Mg (BH₄)₂, Mg₂Ni]), lithium, sodium, aluminum, and transition metals such as nickel, lanthanum, titanium, and iron.

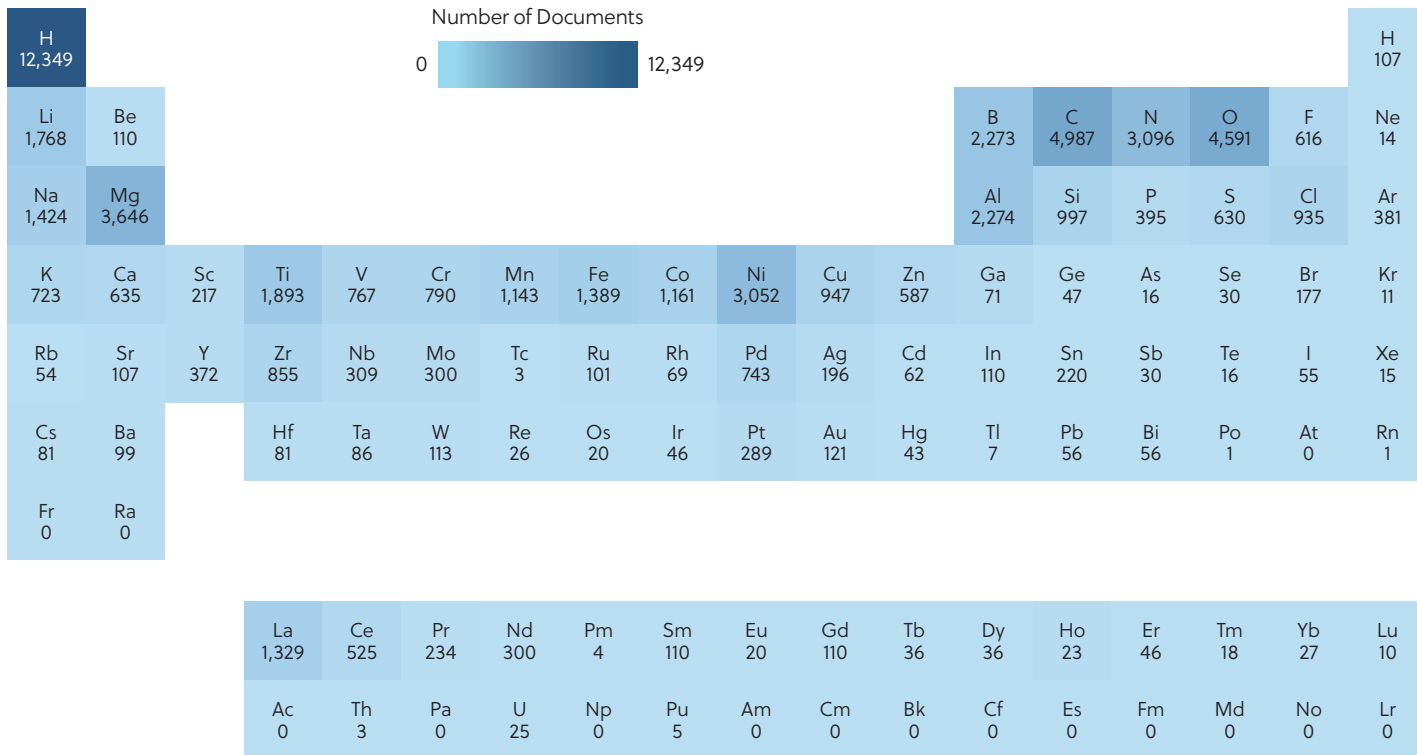


Figure 9. Occurrence of elements in materials used for hydrogen storage research by the number of documents from 2011-2021

Hydrogen fuel cells

Hydrogen fuel cells are the subject of active ongoing research.^{21,119} This was emphasized in the literature analysis which indicated intensive investigations into improving performance and durability while lowering costs to make them viable for market applications.

The literature analysis identified a general decrease in research on materials for hydrogen fuel cell devices since 2013 but there is continued interest in oxides, organic/inorganic small molecules, polymers, and alloys (**Figure 7**). Key substances in hydrogen fuel cell research fall into several different categories, including catalyst alloys of cobalt and platinum, which aim to reduce the amount of platinum and thereby lower costs.¹²⁰ At the same time, the research is striving to increase the durability of fuel cells using nanostructures with non-noble metals.¹²⁰ The use of platinum in other alloys is also being reduced using high surface area nanoalloys and nanoparticles.¹²¹

Various elements are being used in fuel cell development, including forms of carbon as alternatives to noble metal catalysts for oxygen reduction reactions (ORR) via non-noble metal-N-C catalysts and high surface area micro/nanostructures.^{122,123} Carbon in the form of graphene is also being used as a catalyst support or to act as an alternative to noble metal catalysts for oxygen reduction reactions.^{124,125} Nickel has been used as an electrode/electrolyte component in SOFC; ORR and/or HOR catalysts. This work has focused on nanostructures, porosity, and single-atom alloys and has included metal foam as a flow distributor in PEMFCs.^{126,127} Research on platinum, the most used and versatile catalyst component, has focused on reducing loading amounts used using nanoalloys, creating micro/nanostructures, and producing new platinum alloy catalysts.^{128,129}

Oxides that are the subject of recent research include Ceria (CeO_2), which is used as an interlayer material between the electrode and electrolyzer to improve contact area in ceramic fuel cells.¹³⁰ Other oxides include silica (SiO_2) used as a template for catalyst synthesis and as a hybrid nanofluid coolant for PEMFC¹³¹ and Titania (TiO_2) which has been used as an ORR catalyst nanocomposite component or catalyst support.¹³² Nickel monoxide (NiO) has been evaluated as part of the ceramic anode or cathode composition for SOFCs¹³³ and yttrium sesquioxide (Y_2O_3) has also been used in SOFCs but as a solid electrolyte dopant or electrode component.¹³⁴ Other oxides that have been investigated as SOFC electrolyte or electrode components are yttrium zirconium oxide¹³⁵ and zirconium dioxide (ZrO_2) which have the potential to improve electrode/electrolyte interface and reduce degradation.¹³⁶

A further category of materials of interest in research to improve hydrogen fuel cell performance are polymers. These may improve proton-conducting membranes and durability and include ethene, homopolymer,¹³⁷ poly(vinylidene fluoride),¹³⁸ polypropylene¹³⁹ and polytetrafluoroethylene.¹⁴⁰

The occurrence of elements in materials used for fuel cell device research is given in **Figure 10**. This highlights hydrogen (as fuel), oxygen (as oxides in electrodes), and platinum, nickel, nitrogen, iron, and carbon (as a catalyst) which are all basic components of fuel cells. In addition, cobalt, lanthanum and strontium were also frequently found since these are components of perovskite – a class of common research materials used in both electrodes and electrolytes in SOFCs. Cerium was also found frequently as it is an important component of ceramic fuel cells.

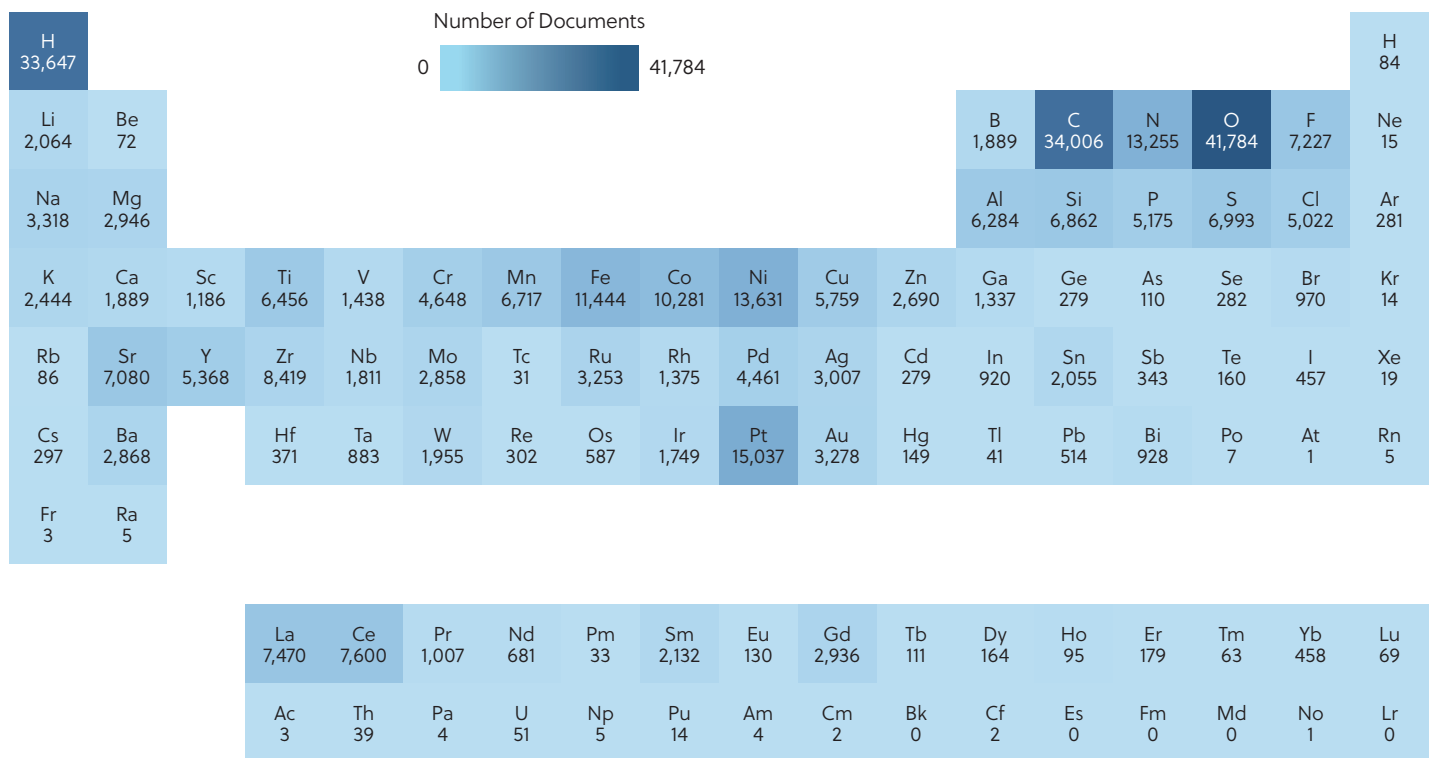


Figure 10. Occurrence of elements in materials used for hydrogen fuel cell device research by the number of documents from 2011-2021



Conclusions and outlook

The analysis of literature from 2011-2021 shows that of the three areas in GHE research, green hydrogen production had the greatest volume of publications and patents. Hydrogen storage and hydrogen fuel cells, however, showed initial decreases in publication followed by later increases with notably increasing proportions of patents. Increasing patent volumes over the decade suggest that hydrogen storage and fuel cells are more technologically mature than green hydrogen production, whose proportion of patents has yet to reach 20%. Green hydrogen production mostly showed increases in the diversity of catalytic materials while hydrogen storage and fuel cells narrowed in the range of materials. The trends in publications and patent volume, suggest that hydrogen storage and fuel cells have been focusing on potentially commercially viable materials, whereas green hydrogen production is still at an exploratory stage.

It is notable that the developments in GHE technology have been mostly confined to a small number of countries, particularly China and that patents have been filed by a limited number of corporations, particularly the Japanese, Chinese, and Korean automobile, appliance, and electronics sectors. This may be of concern to multiple governments elsewhere who have committed to net-zero carbon emissions by 2050³³ but may not be providing sufficient support to research and development in sustainable energy sources such as green hydrogen.¹⁴¹ Greater investment in the GHE is hampered by the current much higher cost of hydrogen versus methane, but this could be addressed with greater funding to help innovation, hydrogen price support and lowering carbon emission limits.¹⁴²

Whilst much research and development effort has gone into green hydrogen technology over the past decade, making the GHE a reality which will enable hydrogen to become a widely used fuel is a tall order. Challenges identified in the literature analysis are the development of more efficient catalysts, hydrogen storage materials and the dehydrogenation process all of which must be green, easy to make, and inexpensive. This is problematic because the current methods for the generation of hydrogen and creating storage materials are energy-intensive processes, and these must be powered by sustainable means. It will also be necessary to select elements/compounds/materials for use in hydrogen production/storage and fuel cells that, on the scales that are needed, are non-toxic and are not environmentally damaging to mine or are harmful to water supplies.^{142,143}

To progress the GHE, it will be necessary to create world infrastructures for the delivery and use of hydrogen in industrial, domestic, and transport applications.¹⁴² It will also be necessary to improve public awareness of hydrogen and its safety in use to reduce fear and increase acceptance.¹⁴³ Despite the challenges that remain, the continuing high level of research and development in GHE technologies determined in the literature analysis indicate that hydrogen is likely to be an increasingly important part of global energy strategies in the coming decades.



References

1. The World Bank, 2014, Fossil fuel energy consumption (% of total). <https://data.worldbank.org/indicator/EG.USE.COMM.FO.ZS> (accessed 2022-04-05).
2. Gielen, D.; Boshell, F.; Saygin, D.; Bazilian, M.; Wagner, N.; Gorini, R. The Role Of Renewable Energy In The Global Energy Transformation. *Energy Strategy Reviews*. **2019**, *24*, 38-50.
3. Oliveira, A.; Beswick, R.; Yan, Y. A Green Hydrogen Economy For A Renewable Energy Society. *Curr. Opin. Chem. Eng.* **2021**, *33*, 100701.
4. Sharma, S.; Agarwal, S.; Jain, A., Significance of Hydrogen as Economic and Environmentally Friendly Fuel. *Energies*. **2021**, *14* (21).
5. Heat values of various fuels - World Nuclear Association. <https://world-nuclear.org/information-library/facts-and-figures/heat-values-of-various-fuels.aspx> (accessed 2022-04-05).
6. Santos, A.; Cebola, M.; Santos, D. Towards The Hydrogen Economy—A Review Of The Parameters That Influence The Efficiency Of Alkaline Water Electrolyzers. *Energies*. **2021**, *14* (11), 3193.
7. Brandon, N. P.; Kurban, Z., Clean energy and the hydrogen economy. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*. **2017**, *375* (2098), 201604008.
8. Yue, M.; Lambert, H.; Pahon, E.; Roche, R.; Jemei, S.; Hissel, D. Hydrogen Energy Systems: A Critical Review Of Technologies, Applications, Trends And Challenges. *Renewable Sustainable Energy Rev.* **2021**, *146*, 111180.
9. Wang, S.; Lu, A.; Zhong, C. Hydrogen Production From Water Electrolysis: Role Of Catalysts. *Nano Convergence*. **2021**, *8* (1).
10. Gallandat, N.; Romanowicz, K.; Züttel, A. An Analytical Model For The Electrolyser Performance Derived From Materials Parameters. *Journal of Power and Energy Engineering*. **2017**, *05* (10), 34-49.
11. Norouzi, N. Hydrogen Production In The Light Of Sustainability: A Comparative Study On The Hydrogen Production Technologies Using The Sustainability Index Assessment Method. *Nucl. Eng. Technol.* **2022**, *54* (4), 1288-1294.
12. *Hydrogen Europe - Tech Overview*. https://hydrogeneurope.eu/wp-content/uploads/2021/11/Tech-Overview_Hydrogen-Storage.pdf (accessed 2022-04-06).
13. Ahluwalia, R. K.; Peng, J. K.; Hua, T. Q., Sorbent material property requirements for on-board hydrogen storage for automotive fuel cell systems. *Int. J. Hydrogen Energy*. **2015**, *40* (19), 6373-6390.
14. Roh, H. S.; Hua, T. Q.; Ahluwalia, R. K., Optimization of carbon fiber usage in Type 4 hydrogen storage tanks for fuel cell automobiles. *Int. J. Hydrogen Energy*. **2013**, *38* (29), 12795-12802.
15. Aziz, M. Liquid Hydrogen: A Review On Liquefaction, Storage, Transportation, And Safety. *Energies*. **2021**, *14* (18), 5917.
16. Ahluwalia, R. K.; Peng, J. K.; Roh, H. S.; Hua, T. Q.; Houchins, C.; James, B. D., Supercritical cryo-compressed hydrogen storage for fuel cell electric buses *Int. J. Hydrogen Energy*. **2018**, *43* (22), 10215-10231.
17. Broom, D. P., Hydrogen Storage Materials: *The Characterisation of Their Storage Properties*. 1 ed.; Springer: London, 2011.
18. Mohan, M.; Sharma, V. K.; Kumar, E. A.; Gayathri, V., Hydrogen storage in carbon materials—A review. *Energy Storage*. **2019**, *1* (2), e35.
19. Hua, T. Q.; Ahluwalia, R. K., Off-board regeneration of ammonia borane for use as a hydrogen carrier for automotive fuel cells. *Int. J. Hydrogen Energy*. **2012**, *37* (19), 14382-14392.
20. Ahluwalia, R. K.; Peng, J. K.; Hua, T. Q., Bounding material properties for automotive storage of hydrogen in metal hydrides for low-temperature fuel cells. *Int. J. Hydrogen Energy*. **2014**, *39* (27), 14874-14886.

21. Sharaf, O. Z.; Orhan, M. F., An overview of fuel cell technology: Fundamentals and applications. *Renewable Sustainable Energy Rev.* **2014**, *32*, 810-853.
22. Felseghi, R. A.; Carcadea, E.; Raboaca, M. S.; Trufin, C. N.; Filote, C., Hydrogen Fuel Cell Technology for the Sustainable Future of Stationary Applications. *Energies.* **2019**, *12* (23).
23. Dodds, P. E.; Staffell, I.; Hawkes, A. D.; Li, F.; Grünewald, P.; McDowall, W.; Ekins, P., Hydrogen and fuel cell technologies for heating: A review. *Int. J. Hydrogen Energy.* **2015**, *40* (5), 2065-2083.
24. Breeze, P., Chapter 2 - The Fundamentals of Fuel Cell Operation. In *Fuel Cells*, Breeze, P., Ed. Academic Press: London, **2017**; pp 11-21.
25. Bidault, F.; Middleton, P. H., 4.07 - Alkaline Fuel Cells: Theory and Application. In *Comprehensive Renewable Energy*, Sayigh, A., Ed. Elsevier: **2012**; Vol. 4, pp 179-202.
26. Breeze, P., Chapter 3 - The Alkaline Fuel Cell. In *Fuel Cells*, Academic Press, London, **2017**; pp 23-32.
27. Dicks, A. L., 4.08 - PEM Fuel Cells: Applications. In *Comprehensive Renewable Energy*, Sayigh, A., Ed. Elsevier: **2012**; Vol. 4, pp 203-245.
28. Breeze, P., Chapter 4 - The Proton Exchange Membrane Fuel Cell. In *Fuel Cells*, Academic Press, London, **2017**; pp 33-43.
29. *Hydrogen and Fuel Cell Technologies Office, U.S. Office of Energy Efficiency & Renewable Energy, Comparison of Fuel Cell Technologies.* <https://www.energy.gov/eere/fuelcells/comparison-fuel-cell-technologies> (accessed 2022-04-06)
30. Breeze, P., Chapter 5 - The Phosphoric Acid Fuel Cell. In *Fuel Cells*, Academic Press, London, **2017**; pp 45-51.
31. Tesfai, A.; Irvine, J. T. S., 4.10 - Solid Oxide Fuel Cells: Theory and Materials. In *Comprehensive Renewable Energy*, Sayigh, A., Ed. Elsevier: Oxford, **2012**; pp 261-276.
32. Breeze, P., Chapter 7 - The Solid Oxide Fuel Cell. In *Fuel Cells*, Academic Press, London, **2017**; pp 63-73.
33. COP21. 2015. <https://unfccc.int/process-and-meetings/conferences/past-conferences/paris-climate-change-conference-november-2015/cop-21> (accessed 2022-04-06).
34. *Hydrogen and Fuel Cell Technologies Office, U.S. Office of Energy Efficiency & Renewable Energy, n.d., Types of Fuel Cells.* <https://www.energy.gov/eere/fuelcells/types-fuel-cells> (accessed 2022-04-06)
35. *Toyota Newsroom, Toyota Introduces Second-Generation Mirai Fuel Cell Electric Vehicle as Design and Technology Flagship Sedan.* **2020.** <https://pressroom.toyota.com/toyota-introduces-second-generation-mirai-fuel-cell-electric-vehicle-as-design-and-technology-flagship-sedan/> (accessed 2022-04-06).
36. *Hyundai Motor Group, Hyundai Motor Group's next-generation fuel cell system, a key technology for popularizing hydrogen energy.* **2021.** <https://tech.hyundaimotorgroup.com/article/hyundai-motor-groups-next-generation-fuel-cell-system-a-keytechnology-for-popularizing-hydrogen-energy/> (accessed 2022-04-06).
37. *Honda, Evolution of Fuel Cell Vehicle.* <https://global.honda/innovation/FuelCell/history.html> (accessed 2022-04-06).
38. *Toyota Newsroom, Toyota Launches Production Model "Sora" FC Bus.* <https://global.toyota/en/newsroom/corporate/21863761.html> (accessed 2022-04-06).
39. *Panasonic Newsroom Global, 2021, Panasonic Launches 5 kW Type Pure Hydrogen Fuel Cell Generator.* **2021.** <https://news.panasonic.com/global/press/data/2021/10/en211001-4/en211001-4.html> (accessed 2022-04-06).
40. *Panasonic Newsroom Global, Panasonic to Demonstrate RE100 Solution Using Pure Hydrogen Fuel Cell Generators.* **2021.** <https://news.panasonic.com/global/press/data/2021/05/en210524-2/en210524-2.html> (accessed 2022-04-06).
41. Zou, X.; Zhang, Y., Noble metal-free hydrogen evolution catalysts for water splitting. *Chem. Soc. Rev.* **2015**, *44* (15), 5148-5180.



42. Li, Z.; Ge, R.; Su, J.; Chen, L., Recent Progress in Low Pt Content Electrocatalysts for Hydrogen Evolution Reaction. *Adv. Mater. Interfaces*. **2020**, *7* (14), 2000396.
43. Zhu, J.; Hu, L.; Zhao, P.; Lee, L. Y. S.; Wong, K.-Y., Recent Advances in Electrocatalytic Hydrogen Evolution Using Nanoparticles. *Chemical Reviews*. **2020**, *120* (2), 851-918.
44. Wang, Q.; Astruc, D., State of the Art and Prospects in Metal–Organic Framework (MOF)-Based and MOF-Derived Nanocatalysis. *Chemical Reviews*. **2020**, *120* (2), 1438-1511.
45. Moon, S. Y.; Gwag, E. H.; Park, J. Y., Hydrogen Generation on Metal/Mesoporous Oxides: The Effects of Hierarchical Structure, Doping, and Co-catalysts. *Energy Technology*. **2018**, *6* (3), 459-469.
46. Gupta, S.; Patel, M. K.; Miotello, A.; Patel, N., Metal Boride-Based Catalysts for Electrochemical Water-Splitting: A Review. *Adv. Funct. Mater.* **2020**, *30* (1), 1906481.
47. Kosco, J.; Bidwell, M.; Cha, H.; Martin, T.; Howells, C. T.; Sachs, M.; Anjum, D. H.; Gonzalez Lopez, S.; Zou, L.; Wadsworth, A.; Zhang, W.; Zhang, L.; Tellam, J.; Sougrat, R.; Laquai, F.; DeLongchamp, D. M.; Durrant, J. R.; McCulloch, I., Enhanced photocatalytic hydrogen evolution from organic semiconductor heterojunction nanoparticles. *Nat. Mater.* **2020**, *19* (5), 559-565.
48. Zhang, T.; Xing, G.; Chen, W.; Chen, L., Porous organic polymers: a promising platform for efficient photocatalysis. *Mater. Chem. Front.* **2020**, *4* (2), 332-353.
49. Jaleh, B.; Nasrollahzadeh, M.; Nasri, A.; Eslamipannah, M.; Moradi, A.; Nezafat, Z., Biopolymer-derived (nano)catalysts for hydrogen evolution via hydrolysis of hydrides and electrochemical and photocatalytic techniques: A review. *Int. J. Biol. Macromol.* **2021**, *182*, 1056-1090.
50. Wang, Q.; Guo, R.; Wang, Z.; Shen, D.; Yu, R.; Luo, K.; Wu, C.; Gu, S., Progress in carbon-based electrocatalyst derived from biomass for the hydrogen evolution reaction. *Fuel*. **2021**, *293*, 120440.
51. Niu, S.; Kong, X.-P.; Li, S.; Zhang, Y.; Wu, J.; Zhao, W.; Xu, P., Low Ru loading RuO₂/(Co,Mn)3O₄ nanocomposite with modulated electronic structure for efficient oxygen evolution reaction in acid. *Applied Catalysis B: Environmental*. **2021**, *297*, 120442.
52. Over, H., Fundamental Studies of Planar Single-Crystalline Oxide Model Electrodes (RuO₂, IrO₂) for Acidic Water Splitting. *ACS Catal.* **2021**, *11* (14), 8848-8871.
53. Wu, Y.-L.; Li, X.; Wei, Y.-S.; Fu, Z.; Wei, W.; Wu, X.-T.; Zhu, Q.-L.; Xu, Q., Ordered Macroporous Superstructure of Nitrogen-Doped Nanoporous Carbon Implanted with Ultrafine Ru Nanoclusters for Efficient pH-Universal Hydrogen Evolution Reaction. *Adv. Mater.* **2021**, *33* (12), 2006965.
54. Chen, K.; Deng, S.; Lu, Y.; Gong, M.; Hu, Y.; Zhao, T.; Shen, T.; Wang, D., Molybdenum-doped titanium dioxide supported low-Pt electrocatalyst for highly efficient and stable hydrogen evolution reaction. *Chin. Chem. Lett.* **2020**, *32*.
55. Nguyen, D. C.; Luyen Doan, T. L.; Prabhakaran, S.; Tran, D. T.; Kim, D. H.; Lee, J. H.; Kim, N. H., Hierarchical Co and Nb dual-doped MoS₂ nanosheets shelled micro-TiO₂ hollow spheres as effective multifunctional electrocatalysts for HER, OER, and ORR. *Nano Energy*. **2021**, *82*, 105750.
56. Jia, Y.; Liu, P.; Wang, Q.; Wu, Y.; Cao, D.; Qiao, Q.-A., Construction of Bi₂S₃-BiOBr nanosheets on TiO₂ NTA as the effective photocatalysts: Pollutant removal, photoelectric conversion and hydrogen generation. *Journal of Colloid and Interface Science*. **2021**, *585*, 459-469.
57. Wang, M.; Cheng, J.; Wang, X.; Hong, X.; Fan, J.; Yu, H., Sulfur-mediated photodeposition synthesis of NiS cocatalyst for boosting H₂-evolution performance of g-C₃N₄ photocatalyst. *Chin. J. Catal.* **2021**, *42* (1), 37-45.
58. Kim, D.; Yong, K., Boron doping induced charge transfer switching of a C₃N₄/ZnO photocatalyst from Z-scheme to type II to enhance photocatalytic hydrogen production. *Applied Catalysis B: Environmental*. **2021**, *282*, 119538.

59. Zhao, D.; Wang, Y.; Dong, C.-L. Huang, Y.-C.; Chen, J.; Xue, F.; Shen, S.; Guo, L., Boron-doped nitrogen-deficient carbon nitride-based Z-scheme heterostructures for photocatalytic overall water splitting. *Nat. Energy*. **2021**, *6* (4), 388-397.
60. Zhuge, K.; Chen, Z.; Yang, Y.; Wang, J.; Shi, Y.; Li, Z., In-situ photodeposition of MoS₂ onto CdS quantum dots for efficient photocatalytic H₂ evolution. *Appl. Surf. Sci.* **2021**, *539*, 148234.
61. Samaniego-Benitez, J. E.; Lartundo-Rojas, L.; García-García, A.; Calderón, H. A.; Mantilla, A., One-step synthesis and photocatalytic behavior for H₂ production from water of ZnS/MoS₂ composite material. *Catal. Today*. **2021**, *360*, 99-105.
62. Liu, X.; Wang, B.; Liu, M.; Liu, S.; Chen, W.; Gao, L.; Li, X., In situ growth of *Appl. Surf. Sci.* **2021**, *554*, 149617.
63. Shi, J.; Qiu, F.; Yuan, W.; Guo, M.; Lu, Z.-H., Nitrogen-doped carbon-decorated yolk-shell CoP@FeCoP micro-polyhedra derived from MOF for efficient overall water splitting. *Chemical Engineering Journal*. **2021**, *403*, 126312.
64. Kuang, P.; Wang, Y.; Zhu, B.; Xia, F.; Tung, C.-W.; Wu, J.; Chen, H. M.; Yu, J., Pt Single Atoms Supported on N-Doped Mesoporous Hollow Carbon Spheres with Enhanced Electrocatalytic H₂-Evolution Activity. *Adv. Mater.* **2021**, *33* (18), 2008599.
65. Riyajuddin, S.; Azmi, K.; Pahuja, M.; Kumar, S.; Maruyama, T.; Bera, C.; Ghosh, K., Super-Hydrophilic Hierarchical Ni-Foam-Graphene-Carbon Nanotubes-Ni₂P-Cu₂P Nano-Architecture as Efficient Electrocatalyst for Overall Water Splitting. *ACS Nano*. **2021**, *15* (3), 5586-5599.
66. Zhang, X.; Zhang, M.; Deng, Y.; Xu, M.; Artiglia, L.; Wen, W.; Gao, R.; Chen, B.; Yao, S.; Zhang, X.; Peng, M.; Yan, J.; Li, A.; Jiang, Z.; Gao, X.; Cao, S.; Yang, C.; Kropf, A. J.; Shi, J.; Xie, J.; Bi, M.; van Bokhoven, J. A.; Li, Y.-W.; Wen, X.; Flytzani-Stephanopoulos, M.; Shi, C.; Zhou, W.; Ma, D., A stable low-temperature H₂-production catalyst by crowding Pt on α -MoC. *Nature*. **2021**, *589* (7842), 396-401.
67. Yoon, H. J.; Hyun Yang, J.; Park, S. J.; Rhee, C. K.; Sohn, Y., Photocatalytic CO₂ reduction and hydrogen production over Pt/Zn-embedded β -Ga₂O₃ nanorods. *Appl. Surf. Sci.* **2021**, *536*, 147753.
68. Shen, R.; He, K.; Zhang, A.; Li, N.; Ng, Y. H.; Zhang, P.; Hu, J.; Li, X., In-situ construction of metallic Ni₃C@Ni core-shell cocatalysts over g-C₃N₄ nanosheets for shell-thickness-dependent photocatalytic H₂ production. *Applied Catalysis B: Environmental*. **2021**, *291*, 120104.
69. Baby, A.; Trovato, L.; Di Valentin, C., Single Atom Catalysts (SAC) trapped in defective and nitrogen-doped graphene supported on metal substrates. *Carbon*. **2021**, *174*, 772-788.
70. Ma, X.; Liu, H.; Yang, W.; Mao, G.; Zheng, L.; Jiang, H.-L., Modulating Coordination Environment of Single-Atom Catalysts and Their Proximity to Photosensitive Units for Boosting MOF Photocatalysis. *J Am Chem Soc.* **2021**, *143* (31), 12220-12229.
71. Kampouri, S.; Ebrahim, F. M.; Fumanal, M.; Nord, M.; Schouwink, P. A.; Elzein, R.; Addou, R.; Herman, G. S.; Smit, B.; Ireland, C. P.; Stylianou, K. C., Enhanced Visible-Light-Driven Hydrogen Production through MOF/MOF Heterojunctions. *ACS Appl. Mater. Interfaces*. **2021**, *13* (12), 14239-14247.
72. Liu, J.; Li, Q.; Xiao, X.; Li, F.; Zhao, C.; Sun, Q.; Qiao, P.; Zhou, J.; Wu, J.; Li, B.; Bao, H.; Jiang, B., Metal-organic frameworks loaded on phosphorus-doped tubular carbon nitride for enhanced photocatalytic hydrogen production and amine oxidation. *J. Colloid Interface Sci.* **2021**, *590*, 1-11.
73. Dai, K.; Zhang, N.; Zhang, L.; Yin, L.; Zhao, Y.; Zhang, B., Self-supported Co/CoO anchored on N-doped carbon composite as bifunctional electrocatalyst for efficient overall water splitting. *Chemical Engineering Journal*. **2021**, *414*, 128804.
74. Cai, Z.-X.; Wang, Z.-L.; Xia, Y.-J.; Lim, H.; Zhou, W.; Taniguchi, A.; Ohtani, M.; Kobihiro, K.; Fujita, T.; Yamauchi, Y., Tailored Catalytic Nanoframes from Metal-Organic Frameworks by Anisotropic Surface Modification and Etching for the Hydrogen Evolution Reaction. *Angewandte Chemie International Edition*. **2021**, *60* (9), 4747-4755.



75. Sankar, S. S.; Keerthana, G.; Manjula, K.; Sharad, J. H.; Kundu, S., Electrospun Fe-Incorporated ZIF-67 Nanofibers for Effective Electrocatalytic Water Splitting. *Inorg. Chem.* **2021**, *60* (6), 4034-4046.
76. Hatami, E.; Toghraei, A.; Barati Darband, G., Electrodeposition of Ni-Fe micro/nano urchin-like structure as an efficient electrocatalyst for overall water splitting. *Int. J. Hydrogen Energy.* **2021**, *46* (14), 9394-9405.
77. Hao, W.; Yao, D.; Xu, Q.; Wang, R.; Zhang, C.; Guo, Y.; Sun, R.; Huang, M.; Chen, Z., Highly efficient overall-water splitting enabled via grafting boron-inserted Fe-Ni solid solution nanosheets onto unconventional skeleton. *Applied Catalysis B: Environmental.* **2021**, *292*, 120188.
78. Shen, X. Q.; Xiang, K.; Fu, X.-Z.; Luo, J.-L., High active and ultra-stable bifunctional FeNi/CNT electrocatalyst for overall water splitting. *Int. J. Hydrogen Energy.* **2021**, *46* (7), 5398-5402.
79. Ge, Y.; Qin, X.; Li, A.; Deng, Y.; Lin, L.; Zhang, M.; Yu, Q.; Li, S.; Peng, M.; Xu, Y.; Zhao, X.; Xu, M.; Zhou, W.; Yao, S.; Ma, D., Maximizing the Synergistic Effect of CoNi Catalyst on α -MoC for Robust Hydrogen Production. *J Am Chem Soc.* **2021**, *143* (2), 628-633.
80. Xie, Y.; Feng, C.; Guo, Y.; Li, S.; Guo, C.; Zhang, Y.; Wang, J., MOFs derived carbon nanotubes coated CoNi alloy nanocomposites with N-doped rich-defect and abundant cavity structure as efficient trifunctional electrocatalyst. *Appl. Surf. Sci.* **2021**, *536*, 147786.
81. Dong, J.; Zhang, X.; Huang, J.; Hu, J.; Chen, Z.; Lai, Y., In-situ formation of unsaturated defect sites on converted CoNi alloy/Co-Ni LDH to activate MoS₂ nanosheets for pH-universal hydrogen evolution reaction. *Chemical Engineering Journal.* **2021**, *412*, 128556.
82. Gu, X.; Chen, Z.; Li, Y.; Wu, J.; Wang, X.; Huang, H.; Liu, Y.; Dong, B.; Shao, M.; Kang, Z., Polyaniline/Carbon Dots Composite as a Highly Efficient Metal-Free Dual-Functional Photoassisted Electrocatalyst for Overall Water Splitting. *ACS Appl. Mater. Interfaces.* **2021**, *13* (21), 24814-24823.
83. El-Bery, H. M.; Salah, M. R.; Ahmed, S. M.; Soliman, S. A., Efficient non-metal based conducting polymers for photocatalytic hydrogen production: comparative study between polyaniline, polypyrrole and PEDOT. *RSC Adv.* **2021**, *11* (22), 13229-13244.
84. Sharma, S.; Kumar, D.; Khare, N., Three-dimensional hierarchical PANI/Bi₂S₃ nanoflowers heterojunction for enhanced photoelectrochemical water splitting. *J. Alloys Compd.* **2021**, *865*, 158779.
85. Zhao, D.; Dai, M.; Liu, H.; Zhu, X.; Wu, X., PPy film anchored on ZnCo₂O₄ nanowires facilitating efficient bifunctional electrocatalysis. *Mater. Today Energy.* **2021**, *20*, 100637.
86. Rasouli, H.; Hosseini, M. G.; Hosseini, M. M., Ta₂O₅-incorporated in photoinduced electrocatalyst of TiO₂-RuO₂ decorated by PPy-NrGO nanocomposite for boosting overall water splitting. *J. Colloid Interface Sci.* **2021**, *582*, 254-269.
87. Zhu, Q.; Qu, Y.; Liu, D.; Ng, K. W.; Pan, H., Two-Dimensional Layered Materials: High-Efficient Electrocatalysts for Hydrogen Evolution Reaction. *ACS Appl. Nano Mater.* **2020**, *3* (7), 6270-6296.
88. Rao, V. N.; Reddy, N. L.; Kumari, M. M.; Cheralathan, K. K.; Ravi, P.; Sathish, M.; Neppolian, B.; Reddy, K. R.; Shetti, N. P.; Prathap, P.; Aminabhavi, T. M.; Shankar, M. V., Sustainable hydrogen production for the greener environment by quantum dots-based efficient photocatalysts: A review. *J. Environ. Manage.* **2019**, *248*, 109246.
89. Zhang, H.-X.; Li, Y.; Li, M.-Y.; Zhang, H.; Zhang, J., Boosting electrocatalytic hydrogen evolution by plasmon-driven hot-electron excitation. *Nanoscale.* **2018**, *10* (5), 2236-2241.
90. Kwon, T.; Jun, M.; Joo, J.; Lee, K., Nanoscale hetero-interfaces between metals and metal compounds for electrocatalytic applications. *J. Mater. Chem. A* **2019**, *7* (10), 5090-5110.
91. Mizoguchi, H.; Park, S.-W.; Hosono, H., A View on Formation Gap in Transition Metal Hydrides and Its Collapse. *J Am Chem Soc.* **2021**, *143* (30), 11345-11348.
92. Samantaray, S. S.; Anees, P.; Bhaghavathi Parambath, V.; S, R., Graphene supported MgNi alloy nanocomposite as a room temperature hydrogen storage material – Experiments and theoretical insights. *Acta Mater.* **2021**, *215*, 117040.

93. Padhee, S. P.; Roy, A.; Pati, S., Mechanistic insights into efficient reversible hydrogen storage in ferrotitanium. *Int. J. Hydrogen Energy*. **2021**, *46* (1), 906-921.
94. Solymosi, T.; Auer, F.; Dürr, S.; Preuster, P.; Wasserscheid, P., Catalytically activated stainless steel plates for the dehydrogenation of perhydro dibenzyltoluene. *International Int. J. Hydrogen Energy*. **2021**, *46* (70), 34797-34806.
95. Peng, D.; Zhang, Y.; Han, S., Fabrication of Multiple-Phase Magnesium-Based Hydrides with Enhanced Hydrogen Storage Properties by Activating NiS@C and Mg Powder. *ACS Sustainable Chem. Eng.* **2021**, *9* (2), 998-1007.
96. Leng, H.; Pan, Y.; Chou, K.-C., Effect of LiH on hydrogen storage property of MgH₂. *Int. J. Hydrogen Energy*. **2014**, *39*, 13622-13627.
97. Zheng, J.; Liu, M.; Wu, F.; Zhang, L., Enabling easy and efficient hydrogen release below 80 °C from NaBH₄ with multi-hydroxyl xylitol. *Int. J. Hydrogen Energy*. **2021**, *46* (55), 28156-28165
98. Ahluwalia, R. K.; Hua, T. Q.; Peng, J. K., On-board and Off-board performance of hydrogen storage options for light-duty vehicles. *Int. J. Hydrogen Energy*. **2012**, *37* (3), 2891-2910.
99. Sulaiman, N. N.; Ismail, M.; Timmiati, S. N.; Lim, K. L., Improved hydrogen storage performances of LiAlH₄ + Mg(BH₄)₂ composite with TiF₃ addition. *Int. J. Energy Res.* **2021**, *45* (2), 2882-2898.
100. Yuan, J.; Huang, H.; Jiang, Z.; Lv, Y.; Liu, B.; Zhang, B.; Yan, Y.; Wu, Y., Ni-Doped Carbon Nanotube-Mg(BH₄)₂ Composites for Hydrogen Storage. *ACS Appl. Nano Mater.* **2021**, *4* (2), 1604-1612.
101. Jokar, F.; Nguyen, D. D.; Pourkhalil, M.; Pirouzfard, V., Effect of Single- and Multiwall Carbon Nanotubes with Activated Carbon on Hydrogen Storage. *Chem. Eng. Technol.* **2021**, *44* (3), 387-394.
102. Ramirez-Vidal, P.; Canevesi, R. L. S.; Sdanghi, G.; Schaefer, S.; Maranzana, G.; Celzard, A.; Fierro, V., A Step Forward in Understanding the Hydrogen Adsorption and Compression on Activated Carbons. *ACS Appl. Mater. Interfaces.* **2021**, *13* (10), 12562-12574.
103. Morse, J. R.; Zugell, D. A.; Patterson, E.; Baldwin, J. W.; Willauer, H. D., Hydrogenated graphene: Important material properties regarding its application for hydrogen storage *J. Power Sources*. **2021**, *494*, 229734.
104. Yang, K.; Qin, H.; Lv, J.; Yu, R.; Chen, X.; Zhao, Z.; Li, Y.; Zhang, F.; Xia, X.; Fu, Q.; Wang, M., The Effect of Graphite and Fe₂O₃ Addition on Hydrolysis Kinetics of Mg-Based Hydrogen Storage Materials. *Int. J. Photoenergy*. **2021**, *2021*, 6651541.
105. Yang, X.; Hou, Q.; Yu, L.; Zhang, J., Improvement of the hydrogen storage characteristics of MgH₂ with a flake Ni nano-catalyst composite. *Dalton Trans.* **2021**, *50* (5), 1797-1807.
106. Xue, W.; Liu, H.; Mao, B.; Liu, H.; Qiu, M.; Yang, C.; Chen, X.; Sun, Y., Reversible hydrogenation and dehydrogenation of N-ethylcarbazole over bimetallic Pd-Rh catalyst for hydrogen storage. *Chemical Engineering Journal*. **2021**, *421*, 127781.
107. Byun, M.; Kim, H.; Choe, C.; Lim, H., Conceptual feasibility studies for cost-efficient and bi-functional methylcyclohexane dehydrogenation in a membrane reactor for H₂ storage and production. *Energy Convers. Manage.* **2021**, *227*, 113576.
108. Al-Hamed, K. H. M.; Dincer, I., A novel ammonia solid oxide fuel cell-based powering system with on-board hydrogen production for clean locomotives. *Energy*. **2021**, *220*, 119771.
109. Demirci, U. B., Mechanistic insights into the thermal decomposition of ammonia borane, a material studied for chemical hydrogen storage. *Inorg. Chem. Front.* **2021**, *8* (7), 1900-1930.
110. Iglesias, M.; Fernández-Alvarez, F. J., Advances in Nonprecious Metal Homogeneously Catalyzed Formic Acid Dehydrogenation. *Catalysts*. **2021**, *11* (11).
111. Kang, P.-C.; Ou, Y.-S.; Li, G.-L.; Chang, J.-K.; Wang, C.-Y., Room-Temperature Hydrogen Adsorption via Spillover in Pt Nanoparticle-Decorated UiO-66 Nanoparticles: Implications for Hydrogen Storage. *ACS Appl. Nano Mater.* **2021**, *4* (10), 11269-11280.



112. Ren, W.; Zhuang, X.; Liu, Z.; Li, S., Hydrogen adsorption performance of Cu-BTC/graphene aerogel composite: A combined experimental and computational study. *Int. J. Hydrogen Energy*. **2021**, *46* (24), 13097-13105.
113. Suresh, K.; Aulakh, D.; Purewal, J.; Siegel, D. J.; Veenstra, M.; Matzger, A. J., Optimizing Hydrogen Storage in MOFs through Engineering of Crystal Morphology and Control of Crystal Size. *J Am Chem Soc*. **2021**, *143* (28), 10727-10734.
114. Mojica-Sánchez, J. P.; Zarate-López, T. I.; Flores-Álvarez, J. M.; Reyes-Gómez, J.; Pineda-Urbina, K.; Gómez-Sandoval, Z., Magnesium oxide clusters as promising candidates for hydrogen storage. *Phys. Chem. Chem. Phys*. **2019**, *21* (41), 23102-23110.
115. Wang, K.; Zhang, X.; Liu, Y.; Ren, Z.; Zhang, X.; Hu, J.; Gao, M.; Pan, H., Graphene-induced growth of N-doped niobium pentaoxide nanorods with high catalytic activity for hydrogen storage in MgH₂. *Chemical Engineering Journal*. **2021**, *406*, 126831.
116. Nathanson, A. S.; Ploszajski, A. R.; Billing, M.; Cook, J. P.; Jenkins, D. W. K.; Headen, T. F.; Kurban, Z.; Lovell, A.; Bennington, S. M., Ammonia borane–polyethylene oxide composite materials for solid hydrogen storage. *J. Mater. Chem. A* **2015**, *3* (7), 3683-3691.
117. Saha, S. S., W.; Kim, N. H.; Lee, J. H., Fabrication of impermeable dense architecture containing covalently stitched graphene oxide/boron nitride hybrid nanofiller reinforced semi-interpenetrating network for hydrogen gas barrier applications. *J. Mater. Chem. A* **2022**, *10*, 4376-4391.
118. Broom, D. P.; Webb, C. J.; Fanourgakis, G. S.; Froudakis, G. E.; Trikalitis, P. N.; Hirscher, M., Concepts for improving hydrogen storage in nanoporous materials. *Int. J. Hydrogen Energy*. **2019**, *44* (15), 7768-7779.
119. U.S. Department of Energy, 2020, *Challenges*. https://www.fueleconomy.gov/feg/fcv_challenges.shtml (accessed 2022-04-07).
120. Wu, Z. P.; Caracciolo, D. T.; Maswadeh, Y.; Wen, J. G.; Kong, Z. J.; Shan, S. Y.; Vargas, J. A.; Yan, S.; Hopkins, E.; Park, K.; Sharma, A.; Ren, Y.; Petkov, V.; Wang, L. C.; Zhong, C. J., Alloying-realloying enabled high durability for Pt-Pd-3d-transition metal nanoparticle fuel cell catalysts. *Nat. Commun*. **2021**, *12* (1).
121. Pavlets, A. S.; Alekseenko, A. A.; Tabachkova, N. Y.; Safronenko, O. I.; Nikulin, A. Y.; Alekseenko, D. V.; Guterman, V. E., A novel strategy for the synthesis of Pt–Cu uneven nanoparticles as an efficient electrocatalyst toward oxygen reduction. *Int. J. Hydrogen Energy*. **2021**, *46* (7), 5355-5368.
122. Y.; Zhu, M.; Luo, X.; Wu, G.; Chao, T.; Qu, Y.; Zhou, F.; Sun, R.; Han, X.; Li, H.; Jiang, B.; Wu, Y.; Hong, X., Coplanar Pt/C Nanomeshes with Ultrastable Oxygen Reduction Performance in Fuel Cells. *Angewandte Chemie International Edition*. **2021**, *60* (12), 6533-6538.
123. Su, C.; Liu, Y.; Luo, Z.; Veder, J.-P.; Zhong, Y.; Jiang, S. P.; Shao, Z., Defects-rich porous carbon microspheres as green electrocatalysts for efficient and stable oxygen-reduction reaction over a wide range of pH values. *Chemical Engineering Journal*. **2021**, *406*, 126883.
124. Mousavi, S. A.; Mehrpooya, M., Fabrication of copper centered metal organic framework and nitrogen, sulfur dual doped graphene oxide composite as a novel electrocatalyst for oxygen reduction reaction. *Energy*. **2021**, *214*, 119053.
125. Kakaei, K.; Ghadimi, G., A green method for Nitrogen-doped graphene and its application for oxygen reduction reaction in alkaline media. *Materials Technology*. **2021**, *36* (1), 46-53.
126. Moriau, L. J.; Hrnjić, A.; Pavličič, A.; Kamšek, A. R.; Petek, U.; Ruiz-Zepeda, F.; Šala, M.; Pavko, L.; Šelih, V. S.; Bele, M.; Jovanovič, P.; Gatalo, M.; Hodnik, N., Resolving the nanoparticles' structure-property relationships at the atomic level: a study of Pt-based electrocatalysts. *IScience*. **2021**, *24* (2), 102102.
127. Wan, Z.; Sun, Y.; Yang, C.; Kong, X.; Yan, H.; Chen, X.; Huang, T.; Wang, X., Experimental performance investigation on the arrangement of metal foam as flow distributors in proton exchange membrane fuel cell. *Energy Convers. Manage*. **2021**, *231*, 113846.

128. Li, S.; Tian, Z. Q.; Liu, Y.; Jang, Z.; Hasan, S. W.; Chen, X.; Tsiakaras, P.; Shen, P. K., Hierarchically skeletal multi-layered Pt-Ni nanocrystals for highly efficient oxygen reduction and methanol oxidation reactions. *Chin. J. Catal.* **2021**, *42* (4), 648-657.
129. Gao, R.; Wang, J.; Huang, Z.-F.; Zhang, R.; Wang, W.; Pan, L.; Zhang, J.; Zhu, W.; Zhang, X.; Shi, C.; Lim, J.; Zou, J.-J., Pt/Fe₂O₃ with Pt-Fe pair sites as a catalyst for oxygen reduction with ultralow Pt loading. *Nat. Energy.* **2021**, *6* (6), 614-623.
130. Le, L. Q.; Hernandez, C. H.; Rodriguez, M. H.; Zhu, L.; Duan, C.; Ding, H.; O'Hayre, R. P.; Sullivan, N. P., Proton-conducting ceramic fuel cells: Scale up and stack integration. *J. Power Sources.* **2021**, *482*, 228868.
131. Bisht, S.; Balaguru, S.; Ramachandran, S. K.; Gangasalam, A.; Kweon, J., Proton exchange composite membranes comprising SiO₂, sulfonated SiO₂, and metal-organic frameworks loaded in SPEEK polymer for fuel cell applications. *J. Appl. Polym. Sci.* **2021**, *138* (22), 50530.
132. Parse, H.; Patil, I. M.; Swami, A. S.; Kakade, B. A., TiO₂-Decorated Titanium Carbide MXene co-Doped with Nitrogen and Sulfur for Oxygen Electroreduction. *ACS Appl. Nano Mater.* **2021**, *4* (2), 1094-1103.
133. Amaya-Dueñas, D.-M.; Chen, G.; Weidenkaff, A.; Sata, N.; Han, F.; Biswas, I.; Costa, R.; Friedrich, K. A., A-site deficient chromite with in situ Ni exsolution as a fuel electrode for solid oxide cells (SOCs). *J. Mater. Chem. A* **2021**, *9* (9), 5685-5701.
134. Sciazko, A.; Shimura, T.; Komatsu, Y.; Shikazono, N., Ni-GDC and Ni-YSZ electrodes operated in solid oxide electrolysis and fuel cell modes. *J. Therm. Sci. Technol.* **2021**, *16* (1), 1-10.
135. Wang, W.; Zhang, X.; Khan, K.; Wu, H.; Zhang, D.; Yang, Y.; Jiang, Y.; Lin, B., Enhanced ORR activity of A-site deficiency engineered BaCo_{0.4}Fe_{0.4}Zr_{0.1}Y_{0.1}O_{3-δ} cathode in practical YSZ fuel cells. *Int. J. Hydrogen Energy.* **2021**, *46* (7), 5593-5603.
136. Zhu, Z.; Gong, Z.; Qu, P.; Li, Z.; Rasaki, S. A.; Liu, Z.; Wang, P.; Liu, C.; Lao, C.; Chen, Z., Additive manufacturing of thin electrolyte layers via inkjet printing of highly-stable ceramic inks. *J. Adv. Ceram.* **2021**, *10* (2), 279-290.
137. Biancolli, A. L. G.; Barbosa, A. S.; Kodama, Y.; de Sousa, R. R.; Lanfredi, A. J. C.; Fonseca, F. C.; Rey, J. F. Q.; Santiago, E. I., Unveiling the influence of radiation-induced grafting methods on the properties of polyethylene-based anion-exchange membranes for alkaline fuel cells. *J. Power Sources.* **2021**, *512*, 230484.
138. Rath, R.; Kumar, P.; Unnikrishnan, L.; Mohanty, S.; Nayak, S. K., Functionalized poly(vinylidene fluoride) for selective proton-conducting membranes. *Mater. Chem. Phys.* **2021**, *260*, 124148.
139. Ayotunde Alo, O.; Olatunji Otunniyi, I.; Pienaar, H.; Rotimi Sadiku, E., Electrical and mechanical properties of polypropylene/epoxy blend-graphite/carbon black composite for proton exchange membrane fuel cell bipolar plate. *Materials Today: Proceedings.* **2021**, *38*, 658-662.
140. Park, G.-C.; Kim, D., Porous PTFE reinforced SPEEK proton exchange membranes for enhanced mechanical, dimensional, and electrochemical stability. *Polymer.* **2021**, *218*, 123506.
141. International Renewable Energy Agency (IRENA) Green hydrogen – A guide to policy making. 2020, https://www.irena.org/-/media/Files/IRENA/Agency/Publication/2020/Nov/IRENA_Green_hydrogen_policy_2020.pdf (accessed 2022-04-07).
142. *Why We Need Green Hydrogen.* 2021, <https://blogs-dev.ei.columbia.edu/2021/01/07/need-green-hydrogen/> (accessed 2022-04-07).
143. Ingaldi, M.; Klimecka-Tatar, D. People'S attitude to energy from hydrogen—from the point of View of modern energy technologies and social responsibility. *Energies.* **2020**, *13* (24), 6495.



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