ENABLING PROGRESS TOWARDS A GREEN HYDROGEN ECONOMY
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. 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. The move to tackle this threat facing the planet will require alternative energy sources with safe and reliable means of conversion, storage and usage. 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). 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 (10-50 kJg⁻¹) alongside the absence of carbon emissions. 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. 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. 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 H₂ storage which improve the energy density of hydrogen must be developed. 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.

Introduction
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$_2$O 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.\(^9\)

\begin{align*}
\text{HER: } & 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2 \\
\text{OER: } & \text{H}_2\text{O} \rightarrow \frac{1}{2} \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \\
\text{Overall: } & \text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2
\end{align*}

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, 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. 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).

- **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.

- **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/m$^3$. A 2-mm stainless steel liner is required for storage pressures up to 700 bar.

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).

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**Figure 2. Physical vs. material-based hydrogen storage**

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. 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 ~1000°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 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, H\textsubscript{2} 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.\textsuperscript{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 for H\textsubscript{2}, which can be overcome using cryogenic temperatures.\textsuperscript{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.\textsuperscript{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).\textsuperscript{19,20}

**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.\textsuperscript{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.\textsuperscript{22} It should be noted; however, that fuel cells have issues with durability, which can restrict their usefulness and cost-effectiveness in use.\textsuperscript{23}

Hydrogen fuel cells use a reverse of water electrolysis. A typical fuel cell has a semi-permeable membrane between a porous cathode and anode.\textsuperscript{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.\textsuperscript{22} At the cathode, molecular oxygen combines with the hydrogen protons and electrons to form water (Figure 3).
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. 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.

**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). 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. 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 CO₂ but this is mostly resolved using hydrogen produced via water electrolysis.

**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.

**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. These cells are mostly used for stationary applications and for the production of electrical and thermal energy known as combined heat and power. 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.
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 2050.14

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.

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.
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

<table>
<thead>
<tr>
<th>Country/Region</th>
<th>Green Hydrogen Production</th>
<th>Hydrogen Storage</th>
<th>Hydrogen Fuel Cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>China</td>
<td>24,528</td>
<td>4,829</td>
<td>4,041</td>
</tr>
<tr>
<td>Japan</td>
<td>2,188</td>
<td>405</td>
<td>709</td>
</tr>
<tr>
<td>United States</td>
<td>3,785</td>
<td>356</td>
<td>842</td>
</tr>
<tr>
<td>Korea, Republic of</td>
<td>2,475</td>
<td>218</td>
<td>420</td>
</tr>
<tr>
<td>Germany</td>
<td>1,616</td>
<td>222</td>
<td>326</td>
</tr>
<tr>
<td>India</td>
<td>2,553</td>
<td>75</td>
<td>634</td>
</tr>
</tbody>
</table>

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.\textsuperscript{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.\textsuperscript{39,40}

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

<table>
<thead>
<tr>
<th>Assignee</th>
<th>Number of Patents</th>
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<tbody>
<tr>
<td></td>
<td>Green Hydrogen Production</td>
</tr>
<tr>
<td>Toyota</td>
<td>37</td>
</tr>
<tr>
<td>Honda</td>
<td>22</td>
</tr>
<tr>
<td>Hyundai</td>
<td>7</td>
</tr>
<tr>
<td>Panasonic</td>
<td>21</td>
</tr>
<tr>
<td>Nissan</td>
<td>2</td>
</tr>
<tr>
<td>Bosch</td>
<td>24</td>
</tr>
</tbody>
</table>
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 RuO$_2$ 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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{44} General inorganics and oxides were increasingly applied to green hydrogen production throughout the decade alongside their use as catalyst supports.\textsuperscript{45,46} In addition, polymers began to be studied as components in heterojunction catalysts,\textsuperscript{47} as tunable stand-alone porous photocatalysts (in the case of covalent organic frameworks),\textsuperscript{48} and as precursors to engineered carbonaceous catalyst materials.\textsuperscript{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\textsubscript{2} and TiO\textsubscript{2},\textsuperscript{51-56} which are frequently used in nanocomposite electrocatalysts. General inorganics included C\textsubscript{3}N\textsubscript{4}, which is amenable to vacancy engineering for photocatalysis and MoS\textsubscript{2} which can be used in semiconductor nanosheets for photocatalysis.\textsuperscript{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 combined with nickel to create a foam for in-situ transformations producing active nano-catalyst components and single atom catalysts.\textsuperscript{63-69} Coordination compounds used as green hydrogen catalysts included UiO-66(NH\textsubscript{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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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 years\textsuperscript{87} and can be combined with other materials into nanocomposites with high surface areas that can take advantage of nanoscale effects such as quantum confinement\textsuperscript{88} and surface plasmon resonance,\textsuperscript{89} as well as interfacial effects including the aforementioned semiconductor heterojunctions and Schottky junctions.\textsuperscript{90}
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.
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

<table>
<thead>
<tr>
<th>Substance class</th>
<th>Example substances</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alloys</td>
<td>LaNi&lt;sub&gt;5&lt;/sub&gt;, MgNi&lt;sub&gt;3&lt;/sub&gt;, FeTi&lt;sub&gt;4&lt;/sub&gt; Stainless Steel&lt;sup&gt;24&lt;/sup&gt;</td>
<td>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</td>
</tr>
<tr>
<td>Hydrides</td>
<td>MgH&lt;sub&gt;2&lt;/sub&gt;, LiH, NaBH&lt;sub&gt;4&lt;/sub&gt;, AlH&lt;sub&gt;3&lt;/sub&gt;, LiAlH&lt;sub&gt;4&lt;/sub&gt;, Mg(BH&lt;sub&gt;4&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Prominent hydrogen storage materials function at feasible working temperatures and have a good hydrogen storage capacity. New regeneration method for NaBH&lt;sub&gt;4&lt;/sub&gt; could enable greater use</td>
</tr>
<tr>
<td>Elements</td>
<td>Carbon, Graphene, Graphite, Nickel</td>
<td>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</td>
</tr>
<tr>
<td>Small organics</td>
<td>9-ethylcarbazole, Methylcyclohexane, Ammonia, Borane, Formic Acid</td>
<td>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</td>
</tr>
<tr>
<td>Small inorganics</td>
<td>UiO-66(Zr), Triaquμ-[1,3,5-benzenetricarboxylato(3-)]κO1κO'1κO3κO'1][μ3-[1,3,5-benzenetricarboxylato(3-)κO1κO3κO'1]]tricopper</td>
<td>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</td>
</tr>
<tr>
<td>Coordination compounds</td>
<td>Zinc Trisμ-[1,4-benzenedicarboxylato(2-)κO1κO'1]]-m4-oxotetra</td>
<td>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</td>
</tr>
<tr>
<td>Oxides</td>
<td>MgO&lt;sup&gt;146&lt;/sup&gt;, Nb&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;&lt;sup&gt;15&lt;/sup&gt;</td>
<td>Thermochemical storage using a reversible metal oxide redox cycle with hydrogen as a reducing agent and H&lt;sub&gt;2&lt;/sub&gt;O as an oxidizing agent. The best hydrogen storage oxides such as Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;, GeO&lt;sub&gt;2&lt;/sub&gt;, MoO&lt;sub&gt;2&lt;/sub&gt;, SnO&lt;sub&gt;2&lt;/sub&gt;, ZnO, and WO&lt;sub&gt;3&lt;/sub&gt; are supported with Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;, TiO&lt;sub&gt;2&lt;/sub&gt;, Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;, MnO, and MgO</td>
</tr>
<tr>
<td>Polymers</td>
<td>Polyethylene Glycol, Nylon 6&lt;sup&gt;157&lt;/sup&gt;</td>
<td>Porous organic polymers, hyper-crosslinked polymers, and polymers with intrinsic microporosity reversibly store and release hydrogen through physisorption on their highly porous structures</td>
</tr>
<tr>
<td>Nanomaterials</td>
<td>Carbon and Boron Nitride Nanotubes, Metal Hydride Nanoparticles, Complex Hydride/Carbon Nanoclusters&lt;sup&gt;118&lt;/sup&gt;</td>
<td>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</td>
</tr>
</tbody>
</table>
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 \([\text{MgH}_2, \text{Mg} (\text{BH}_4)_2, \text{Mg}_2\text{Ni}]\)), 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. Other oxides include silica (SiO$_2$) used as a template for catalyst synthesis and as a hybrid nanofluid coolant for PEMFC and Titania (TiO$_2$) which has been used as an ORR catalyst nanocomposite component or catalyst support. Nickel monoxide (NiO) has been evaluated as part of the ceramic anode or cathode composition for SOFCs and yttrium sesquioxide (Y$_2$O$_3$) has also been used in SOFCs but as a solid electrolyte dopant or electrode component. Other oxides that have been investigated as SOFC electrolyte or electrode components are yttrium zirconium oxide and zirconium dioxide (ZrO$_2$) which have the potential to improve electrode/electrolyte interface and reduce degradation.

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, poly(vinylidene fluoride), polypropylene and polytetrafluoroethylene.

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.
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 2050 but may not be providing sufficient support to research and development in sustainable energy sources such as green hydrogen. 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.

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.

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. It will also be necessary to improve public awareness of hydrogen and its safety in use to reduce fear and increase acceptance. 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


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For more details on the research trends and developments for Green hydrogen economy, see our publication in https://www.cas.org/greenhydrogen
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