# ADVANCES IN HYDROGEN PRODUCTION AND STORAGE

# HYDROGEN ELECTRICA E I G E S

Edited By Mehmet Sankir Nurdan Demirci Sankir





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## Advances in Hydrogen Production and Storage

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# Preface

The decision of 28 countries to limit global warming to well below 2 degrees celsius in accordance with the Paris Agreement, can be realized by minimizing  $CO_2$  emissions, which can only be accomplished by establishing a hydrogen ecosystem. A new geopolitical order is envisaged, in which sectors dealing with energy production, distribution, and storage, and thus an increasing carbon footprint, are reconstructed. In short, an economic order with new tax regulations is being created in which carbon footprints will be followed. This effort, which is called the "Green Deal," is defined in Europe as a new growth strategy aiming for net-zero  $CO_2$  emissions. We know that transportation is responsible for about 24% of all  $CO_2$  emissions. Therefore, any efforts to reduce emissions must include utilizing hydrogen in the transportation sector.

Fuel cells use hydrogen directly in most types of vehicles—from passenger cars to trains—without some of the disadvantages of batteries such as low energy density, high initial costs, and a slow charge. Therefore, the number of hydrogen filling stations required for fuel cells, about one-tenth of the number of fast-charging stations, can meet the same needs as batteries. Additionally, hydrogen charging is at least three times faster. Therefore, it is essential to emphasize that hydrogen-powered transportation is still the most reasonable way to reduce emissions.

As part of our "Advances in Hydrogen Production and Storage" series, this volume covers the cutting-edge technologies used in fuel cell-powered cars. Additionally, it highlights the research efforts presented in the literature while adding a valuable component to the area. It also discusses basic as well as advanced engineering details for both scientists and engineers in academia and industry.

There are seven chapters in the book. Chapter 1 introduces hydrogen and electrical vehicles. Hydrogen storage and compression systems are analyzed in Chapters 2 and 3, respectively. Chapter 4 discusses hydrogen propulsion systems for UAVs. The testing and evaluation of hydrogen fuel cell vehicles are covered in Chapter 5. Chapter 6 focuses on hydrogen production and polymer electrolyte membrane (PEM) fuel cells for electrical vehicles. The final chapter, Chapter 7, covers the issues concerning the power and durability of fuel cell vehicles.

In closing, we wish to thank the distinguished authors for their valuable contributions in reviewing the efforts made towards using hydrogen in electrical vehicles.

Editors

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#### Abstract

Hydrogen usage in electric vehicles is one of the domains which provide immense potential to explore in the race of energy efficient vehicles. As the world continuously moves towards clean and green environment, where all possible measures are been taken to minimize the carbon emission. Discussed here are the following: the numbers of hydrogen-utilized projects for energy, reducing prices of clean energy production facilities, and researching new methods to store hydrogen. Fuel cells which use hydrogen as the source of energy are proving themselves to be a serious candidate in this cause with numerous research are taking place to avail this opportunity.

*Keywords*: Hydrogen electrical vehicles, zero carbon emission, hydrogen storage, green environment, hydrogen production, carbon capture, electrolysis, fuel cells

## 1.1 Hydrogen Usage in Electrical Vehicles

Probably the most crucial and challenging issue the world is facing nowadays is carbon emission. It has effects over several aspects, from environmental problems, power generation, economy, and many others. The world has reached the "no going back" point with carbon emissions, and we have to take effective measures in dealing with this challenge. Luckily, many nations and agencies started to intensify their efforts in order to face this problem. This can be sensed from International's Energy Agency (IEA) "net zero emission by 2050 roadmap" report [1]. IEA plans to make drastic changes to fuel sources and replacing fossil fuels which have a high carbon

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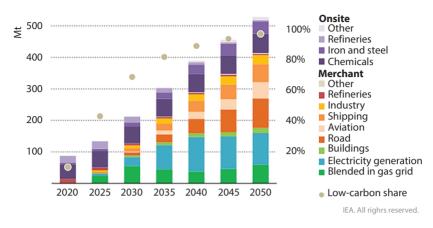


Figure 1.1 Hydrogen as a source of fuel future development plan. (Net Zero by 2050).

emission with hydrogen from pure hydrogen sources such as electrolysis or low carbon hydrogen sources such as methane and ammonia. Figure 1.1 above displays the future development plan for hydrogen usage as a fuel in different sectors.

We can see how the plan is to grow from below 100 Mt to greater than than 500 Mt between 2020 and 2050. We can also notice that using hydrogen as a fuel in transportation also plays a crucial rule in the upcoming years.

Fuel Cell Electric Vehicles (FCEV) uses energy extracted from hydrogen fuel cell as a source of fuel [2]. FCEV has zero carbon emissions, and the only emissions are water and heat. FCEV also has a higher efficiency compared to conventional Internal Combustion Engine (ICE) cars. Thanks to the regenerative braking system, a battery can be connected to brakes in order to store lost energy due to braking and use it elsewhere. FCEV has some advantages over all electric vehicles. First of all, FCEV takes its power from hydrogen tanks, which means it doesn't require long charging times like electric vehicles. Another clear advantage is that FCEV power is dependent on the hydrogen tank size, while electric vehicle's power depends on the size of the battery.

Figure 1.2 below shows the main components of FCEV [3]. A stack of fuel cells provides the required energy extracted from the hydrogen tank, and of course the output of this reaction is energy plus water without any carbon emissions. The battery at the back of the vehicle is connected to the braking system in order to harvest the lost energy due to braking and store it for future use.

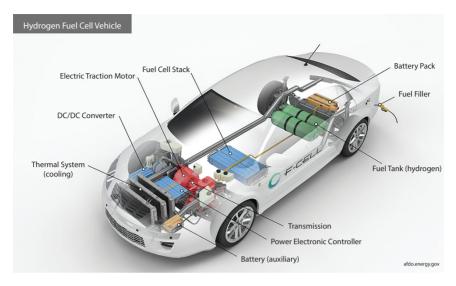
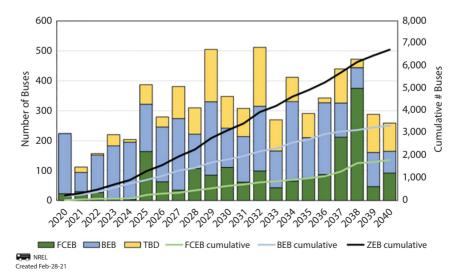


Figure 1.2 Components of FCEV (U.S. Department of Energy).

Bear in mind that FCEV is not only limited to cars. It can be used in busses, trains, or even as a source of power for space missions. The latter is actually very important since the output water can be of great use in space missions where there is no source of water. Figure 1.3 below shows the current and future development of Zero Emission Busses (ZEB) in California, USA.



**Figure 1.3** Current and future development plan for ZEB in California-USA (Fuel Cell Buses in U.S.).

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Region	Number of ZEBs
Europe	1467
Asia	2518
Australia	100
South America	2
Total	4087

**Table 1.1** Current and future development planfor ZEB in regions other than USA (Fuel CellBuses in U.S.).

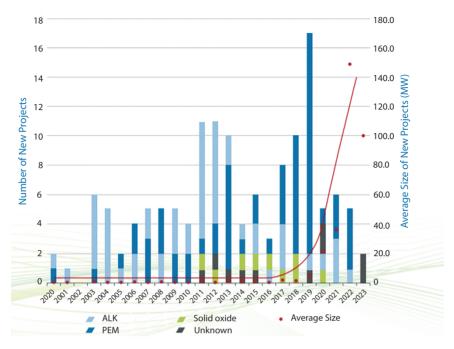
In the USA alone, the estimated number of ZEB between 2020 and 2040 is 7000, between Fuel Cell Electric Busses (FCEB) and Battery Electric Busses (BEB). Table 1.1 above shows the same development plan for regions other than the USA [4].

## 1.2 Hydrogen Production for Electrical Vehicles

Obviously, fuel cells need hydrogen in order to operate, and the process is 100% carbon free. However, the pure hydrogen sources so far haven't been carbon free. In fact, carbon emissions involved in hydrogen production from fossil fuels and coal are matched to and sometimes higher to carbon emissions from IC vehicles [5]. It is not enough to shift into hydrogen as a fuel to cut down carbon emissions. Hydrogen sources should also be carbon free in order to optimize this technology. Germany has proposed a 150 Million EUR project of 100 MW water electrolyzer that uses wind energy in order to produce pure hydrogen from water electrolysis. Producing hydrogen from renewable sources such as wind or solar energy is the key of success for this approach. Netherlands also is studying a 2 GW project similar to Germany. Austria is currently producing pure hydrogen from a 6 MW water electrolyzer. Japan, Canada, China, USA and many other countries are also investing in similar projects.

Figure 1.4 below shows the current status of water electrolysis projects.

An alternative and less costly solution is to use "Blue hydrogen production" which is producing pure hydrogen from fuel fossils with capturing  $CO_2$  emissions. Of course, blue hydrogen is not  $CO_2$  free. In fact,  $CO_2$ 



**Figure 1.4** Current status of water electrolysis projects (Hydrogen: A Renewable Energy Perspective).

capture efficiency is estimated at 85–90% at best. However, it is still a good option to reduce carbon emissions and to provide pure hydrogen for use as a fuel. Figure 1.5 below shows the expected fall of price of electrolyzers between now and 2050.

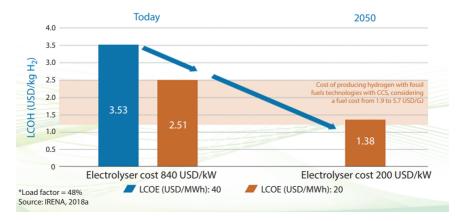


Figure 1.5 Prices of electrolyzers (Hydrogen: A Renewable Energy Perspective).

## 1.3 Hydrogen Storage Methods

Pure hydrogen can be stored in two main methods [6]:

- 1. Physical storage.
- 2. Chemical storage.

Physical storage implies that hydrogen atoms do not interact with the storing medium. It can be either compressed or liquefied cryogenically. Compressed hydrogen can be stored in gas cylinders, stationary storage systems such as underground reservoirs, glass microsphere, pipelines, and other methods.

Chemical storage on the other hand occurs when hydrogen atoms interact with the storage medium. It can be categorized as adsorption, such as adsorption by zeolites and metal-organic materials. It can be also categorized as absorption, such as metal hydrides. Finally, it can also be categorized as chemical interactions with storage materials such as liquid organic hydrides, ammonia and methanol, water reacting metals.

Each of the aforementioned methods has its pros and cons. Storing hydrogen physically is the simplest method. However, it requires a considerable amount of energy to compress the hydrogen or liquefy it. Chemical storage methods are effective, but still under development in order to optimize an efficient way to store pure hydrogen for usage as a fuel.

## 1.4 State-of-the-Art for Hydrogen Generation and Usage for Electrical Vehicles

Xu *et al.* [7] designed a liquid hydrogen storage tank to be used in remotely operated aircraft which will have increased endurance and will fly at high altitude. The work reported the basic structural design and analysis of the cryogenic liquid hydrogen tank, a thermal model was established for the tank and heat leakage of the support system was reduced by building insulating support. The result obtained shows the feasibility of the design and analysis method with stable structure and required mechanical strength.

Aceves *et al.* [8], showed that the cryogenic capable pressure vessels integrated within a cryo-compressed storage system can store high-density hydrogen, they have high thermal endurance compared to conventional liquid hydrogen tanks, and can improve the evaporative losses in automobiles. The developed system store hydrogen more efficiently, provide fast

refueling, and are light in weight. The system developed was demonstrated on the hydrogen hybrid vehicle which enhanced the driving range on a single fuel tank with high thermal endurance.

Okumus *et al.* [9], developed a hydrogen generation system (HGS) using borohydride and a fuel cell system (FCS) to power and manufacture an unmanned aerial vehicle (UAV). The research works on preparing an economical and durable hydrogen generation catalyst through sodium borohydride solution by keeping it under high pressure in the reaction chamber and by controlling the flow rate of the fuel pump and heating device power. While for the fuel cell system of the UAV, a high-rate hydrogen generation system catalytic hydrolysis of NaBH<sub>4</sub> through transition metal catalysts was developed. The developed HGS and FCS generate 218 W power and show an energy density value of about 325 Wh/kg.

Ahluwalia *et al.* [10] performed the technical assessment of the onboard and off-board performance of cryo-compressed hydrogen storage tank which will be used in automotive applications. The on-board performance assessment includes weight, volume energetics, and refueling while the offboard assessment includes thermal management greenhouse gas emissions and energy efficiency, etc. The works show that a cryo-compressed storage system has the potential to meet the required target which has the appropriate gravimetric capacity, volumetric capacity, and in control hydrogen loss during dormancy under certain conditions of minimum daily driving.

Yamashita *et al.* [11], reported the manufacturing of a high-pressure hydrogen storage system which will be used in Toyota Mirai. The new hydrogen storage system used incorporated new components such as valves, regulators, and tanks which will provide increased hydrogen capacity without compromising on the interior space. The weight of the new storage system was reduced by using improved Carbon fiber reinforced plastic (CFRP) and refueling performance was also improved on the developed hydrogen storage system by ensuring compatibility with the SAE J2601 and J2799 standards for communication between the hydrogen station and vehicle.

Zhang *et al.* [12], presented a thorough system design and control strategy of the vehicles that are utilizing hydrogen energy. The work presented hydrogen supply, hydrogen storage method, safety protocols of the hydrogen vehicle system. In the hydrogen vehicle, three different types of the fuel storage system are used for a brief period, that are high pressure, liquid storage, and metal oxide storage system to see compare performance. Proton exchange membrane fuel cell (PEMFC) is used as fuel cells and the driving form and intelligent control of the PEMFC hybrid vehicle are analyzed.

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Gany *et al.* [13], showed the benefits of utilizing electric power and using onboard hydrogen generation storage for marine vehicles. Aluminumwater reaction is carried out for the generation of hydrogen and electric energy vehicles, the method used shows a high reaction rate and increased hydrogen production at room temperature. The use of this storage system with PEM fuel cell provides a compact method for electrical energy storage which was feasible for long duration and long-range. A model boat equipped with a hydrogen reactor, fuel cell, and electric motor has been constructed and operated, demonstrating the technology.

Ananthachar *et al.* [14], showed the comparison of energy efficiencies of different types of the hydrogen storage system used in a fuel cell vehicle, the work also analyzed the reformer system in a fuel cell vehicle. Three of the most used fuel storage methods on fuel cell vehicle were compared which includes (a) compressed hydrogen gas storage, (b) metal hydride storage, and (c) onboard methanol-reformer system. The compressed hydrogen gas stored fuel cell vehicle was concluded to be the most energy-efficient vehicle. The compressed hydrogen gas tank vehicle storage at 33% is either slightly above or equal to the battery-electric car depending on the source of fuel in the power plant producing electricity for the battery charging. The compressed gas system is simple in design; lighter in weight compared to the other system, and is far more energy-efficient.

Deluchi *et al.* [15], showed an analysis of the performance, technology, safety, and environmental aspects of the solar-hydrogen fuel cell vehicles, a fuel cycle where hydrogen is generated by the solar-electrolysis of water and after that used in a fuel-cell-powered electric motor vehicle. The developed vehicle will produce very little pollution. Hydrogen fuel cell vehicle shows the best feature from both battery-powered and fossil fuel vehicles, which includes zero-emission, quiet operation, high efficiency, fast refueling time, and long life with long-range.

## 1.5 Conclusions

In short, in the year of 2022 it is possible to say that Hydrogen is the next wave for electrical vehicles due to its numerous advantages. Therefore in very near future Hydrogen will play the key role in the mobility which uses renewable energy systems. Recently the fuel cell research and its industrial applications gained enormous momentum and one of the best ways to use the hydrogen as energy source is to build smart fuel cell systems having high energy efficiency and zero  $CO_2$  emission. Using of such systems will serve the decarbonization both in industry and transport. In addition, it

is envisaged that in near future fuel cells may complement batteries and supercapacitors to decarbonize energy storage systems. By this in case of transportation it is possible to predict that in about 50 years zero emission vehicles will be mobile on the roads. Further Hydrogen busses and trucks, and fuel cell trains (hydrail) are next applicable vehicles having heavy loads and long distances.

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# Study on a New Hydrogen Storage System – Performance, Permeation, and Filling/Refilling

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#### Abstract

Hydrogen is increasingly a possibility to replace fossil fuels in vehicle propulsion. However, due to the properties of H<sub>2</sub>, there are still unsolved difficulties for such replacement. This chapter presents a new way for H<sub>2</sub> storage in vehicles, propelled either by reciprocating engines or by stacks of fuel cells – H<sub>2</sub> is at high pressure within small spheres randomly packed in conventional vehicle's tanks. The H<sub>2</sub> supply by the spheres to the consumer or the refilling of such spheres is controlled by a chip. The purpose of this study is to evaluate the performance of the new system, comparing it with conventional fuel storage systems through parameters such as the energy stored by volume (VED) and the gravimetric energy density (GED); moreover, to evaluate the H<sub>2</sub> leaks by permeation and see which is the best set of materials for each part of the system; to check the compliance of the system with safety standards; finally, to propose a plausible method for the filling/refilling of spheres. It was concluded that GED is threefold and VED is about half the homologous values of conventional systems. To guarantee safety, the spheres were built with two concentric layers, aluminum for the liner and CFEP for the structural layer, Si for the chip, and aluminum for the tank.

*Keywords*: Hydrogen, permeation, storage safety, energy systems, green energy, vehicle propulsion, packing factor, envelope tank

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## 2.1 Introduction

Around 87% of worldwide man-generated  $CO_2$  emissions are due to fossil fuel combustion [1]. In the last few years, governments of several countries have shown great interest to implement an effective worldwide plan to halt the global warming of the Earth and tackle the challenges linked to climate change [2]. This effort was patent in the Paris Agreement, which aims to decarbonize the world economies [3]. However, the goals imposed by the Paris Agreement jeopardize the reduction of energy poverty and, therefore, have been questioned [4].

In the path for decarbonization, it is foreseen that hydrogen  $(H_2)$  will be considered an important energy vector, either for energy storage or for propulsion [2, 5, 7]; some experts foresee that, in the future,  $H_2$  will be used as a general-purpose energy vector, either for energy storing or transport [5, 6]. The most economically powerful countries like, for example, China, [8–10], Germany [11], Japan [12] and the United States [13], are getting ready to boost the consumption of  $H_2$ , which is shown by their leader's preparedness to build a friendly economic and political background.

Energy solutions are seen as the way forward for a sustainable future; several authors have started to study earnestly this subject [4, 14, 15]. Dincer and Acar [14] claim that smart energy is associated with solutions involving  $H_2$ . These authors highlight the importance of a carbon-free economy, where sustainable  $H_2$  production is still under development. They stated, as well, that the minimum and necessary requirements for an intelligent solution based on  $H_2$  towards a sustainable future are: (i) use of renewable energy and its control, (ii) energy conservation, (iii) clean energy, (iv) the use of smart grids and (v) storage of energy carriers and more efficient chemical species [14].

The use of  $H_2$  as fuel is at an early stage. To go forward, it is necessary to create good infrastructures for storage as well as distribution. Refueling stations must be safe and allow fast refilling to meet the basic and necessary conditions for common use [16, 17].

Soon, for the propulsion of vehicles, stacks of Proton Exchange Membranes Fuel Cells (PEMFC), could be a competitive and ecological alternative to batteries. The  $H_2$  for fuel cells can achieve large-scale use in vehicles as renewable energy becomes widespread [18–20]. One of the main challenges to get this is the improvement of  $H_2$  filling stations, in terms of safety and quick refilling [21].

There is also a rising interest in the use of  $H_2$  for vehicle propulsion through combustion engines.

The storage of  $H_2$  in a vehicle is recognized as of great importance: nearly 70% of publications are about the storage of  $H_2$  [22]. In fact, in consequence of the growing interest in the use of  $H_2$  for vehicle propulsion, the interest for storing this fuel in vehicles has also risen.

There are essentially two ways to store  $H_2$  [6]. The first way is to store it as (i) compressed gas, (ii) cryogenic liquid, (iii) adsorbed on carbon nanofibers, or (iv) adsorbed on a metal, such as a reversible metal hydride [6, 23]. In the second form, hydrogen is combined with certain chemical species to obtain methanol (CH<sub>3</sub>OH), ammonia (NH<sub>3</sub>), etc.

The most common storage method for  $H_2$ , in vehicles or in stationary applications (filling stations, underground caves, and so on...) are the man-made pressurized containers of various shapes and sizes. Larminie *et al.* [23] focus on some advantages over  $H_2$  storage compared to other storage systems. They emphasize CGH<sub>2</sub>, because of its unlimited storage time, simplicity, and no purity requirements.

Other studies have been carried out, such as the environmental impact of using  $H_2$  as a fuel in vehicles, where  $H_2$  powered vehicles are compared with electric vehicles charged with electricity generated by renewable sources, or green energy (sun, wind, tides, among others) [6, 24]. In these research works, reference is made to the great interest in the issue of  $H_2$ storage. They claim that it is economically viable to store large amounts of energy, in the form of  $H_2$ , considering the seasonal availability of green energy [25–28]. In fact, it is possible to use an eventual surplus of renewable energy production to obtain hydrogen that will be stored until it is required by consumers [6, 22–28]. In the case of such surpluses, Tarkowski [29] studied the feasibility of underground hydrogen storage using salt caverns, deep aquifers, depleted gas fields and depleted oil fields.

It is well known that because  $H_2$  has a very low density, to introduce a large mass of gaseous  $H_2$  into a small container, the pressure inside the container must be very high, like 700 daNcm<sup>-2</sup>. In the case of liquid  $H_2$ , the pressure inside the container is usually low, around 3 daNcm<sup>-2</sup>, but the temperature must go down to -252.77°C; and even at such low temperature, the density of  $H_2$  is still very low, 77 kg m<sup>-3</sup> [5, 30].

Crowl and Jo [31] mention the dangers and risks associated with the use of  $H_2$ . They state that danger is linked to explosive and flammable nature and risk is estimated by a combination of the accident consequences together with the probability of the accident happening.

A dangerous feature of the  $H_2$  is its minimal ignition energy, compared to other gases, which means that  $H_2$  is easily ignited. Furthermore, there is also the problem related to the  $H_2$  dangerous wide range of flammability, from 4% to 77% (v/v), and, accordingly, it is important to avoid  $H_2$  in small