The Fundamentals of Hydrogen
FOR ELECTRIC POWER GENERATION

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INTRODUCTION

Technological and regulatory developments in the clean energy sector have occurred rapidly over the past few years. Consequently, the fast-paced release of complex information and jargon can be overwhelming. This white paper will educate readers on the fundamentals of hydrogen as a fuel, and its usage in internal combustion engines and fuel cells for electric power generation.

A sound understanding of the basics of hydrogen technology should enable readers to effectively monitor and comprehend new developments as well as analyze the impact of various regulatory, manufacturing, and supply chain-related factors on the market adoption of this technology.

IMPORTANT FACTS ABOUT HYDROGEN:

H OR H2?

The first element in the periodic table is the hydrogen atom (H). Hydrogen in its atomic form contains one positively charged proton at its center, and one negatively charged electron in the first orbital. Usually (depending on the isotope) the hydrogen atom does not contain a neutron. *Figure 1*

Due to this unpaired electron (the first orbital needs two electrons), hydrogen in its atomic form (H) is unstable. When two hydrogen atoms bond together, they share two electrons in their first orbital thus forming a hydrogen molecule (H_2). Hydrogen in its molecular form (H_2) is stable and therefore it is quite common. Hence, usually it is referred to in its molecular form. *Figure 2*

Figure 1

Single Hydrogen Atom (H)

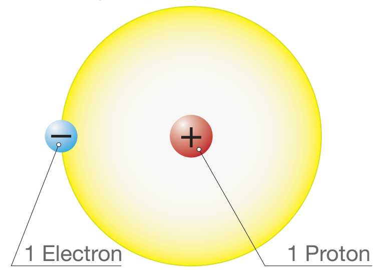
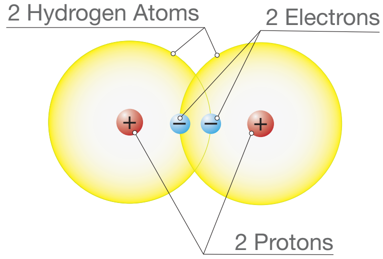


Figure 2

Hydrogen Molecule (H_2)



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WHY SO MUCH INTEREST IN HYDROGEN (H2) FOR ENERGY PRODUCTION?

There are three important reasons why hydrogen is of interest in electric power generation:

1) HYDROGEN IS A POTENT ENERGY CARRIER

As the name suggests, an energy carrier is a mean of temporary storage of energy, which can be transported and later converted to other forms such as mechanical work (e.g., compressed air, hydrogen fueling an internal combustion engine), or heat (e.g., molten salt storage), or electricity (e.g., batteries, hydrogen operating a fuel cell).

On a weight basis, hydrogen has the highest energy content of any common fuel. For example, one pound of hydrogen contains 54.44 MJ of energy versus one pound of diesel contains 20.64 MJ and one pound of gasoline contains 20 MJ of energy. That means, on a weight basis, the energy content of hydrogen is almost three times that of diesel or gasoline.

2) HYDROGEN IS A CLEAN FUEL

When hydrogen (H_2) combines with pure oxygen (electro-chemical process), it produces water and releases energy (e.g., electricity). Thus, this process does not produce any by-products harmful to the environment.

3) HYDROGEN IS ABUNDANTLY AVAILABLE

As previously learned, hydrogen is stable in its molecular form (H_2). However, the bond in the hydrogen molecule isn't that strong. That's why hydrogen does not exist naturally on its own. As a result, it needs to be extracted from various compounds found on earth.

Below are examples of various sources of hydrogen.

Compounds in liquid form: petroleum (a form of hydrocarbon), water

Compounds in gaseous form: natural gas or any methane-rich gas (a form of hydrocarbon)

Compounds in solid form: coal (a form of hydrocarbon), biomass (e.g., wood, manure, crops)

This leads to an important deduction that energy must be spent to extract hydrogen from its various compound forms.

The interesting fact is that it takes more energy to produce hydrogen than it provides as an energy carrier. However, the benefits associated with its abundant availability, high energy content, and clean emissions characteristics overshadow this peculiarity.

HYDROGEN PRODUCTION METHODS—BASIC PRINCIPLES:

With approximately 10 million metric tons of hydrogen produced annually in the United States, the primary consumption has been by ammonia production and petroleum refining industries. However, hydrogen is becoming a subject of interest in many other industries such as transportation, electric power generation, food processing, and manufacturing. Hydrogen can be produced using various processes as listed below.

BIOLOGICAL PROCESS

Microorganisms such as bacteria and microalgae produce hydrogen through biological reactions using sunlight or organic matter.

ELECTROLYTIC PROCESS

In this process, which is widely familiar to all of us, electricity is used to split water into hydrogen and oxygen. In the commercial sector, this process is commonly known as a power-to-gas process.

Note that the process of electrolysis by itself does not produce any harmful emissions. If the electricity used for electrolysis is from clean renewable sources such as wind, solar, etc. then the hydrogen produced would be considered "green."

However, if the electricity was derived from fossil fuels (contain hydrocarbons) or the combustion of even renewable biomass (e.g., wood, manure, crops) then carbon dioxide emissions would be indirectly associated with that electrolytic process. In such cases, hydrogen production via electrolysis would not be considered "green."

DIRECT SOLAR WATER-SPLITTING PROCESS (PHOTOLYTIC PROCESS)

In this case, solar energy is used to split water into hydrogen and oxygen.

HYDROGEN PRODUCTION METHODS—BASIC PRINCIPLES (CONT.):

THERMOCHEMICAL PROCESS

As the name suggests, this process uses heat and chemical reactions to release hydrogen from organic materials such as fossil fuels and biomass.

The steam methane reforming (SMR) process can be classified as a thermochemical process. SMR accounts for most of the commercially produced hydrogen in the United States. In the SMR process, high pressure (43 to 362 PSI) and high-temperature steam (1292 to 1832°F) is used in the presence of a catalyst to separate hydrogen from a methane (CH_4) source. Natural gas is commonly used in this process because of its high methane content and wide availability. The by-products of this process are carbon monoxide (CO) and a relatively small amount of carbon dioxide (CO_2).

Steam methane reforming is primarily an endothermic process as it requires a lot of heat for the desired chemical reaction to take place:
$CH_4 + H_2O$ (+ heat) –> $CO + 3H_2$

Food for thought: Natural gas is already a good source of fuel. However, it's not renewable. Also, being a fossil fuel, it contains hydrocarbons. So, carbon dioxide released in the reformation process does add to the greenhouse effect.

For hydrogen production, would biomass be a better option as it's a renewable source? For hydrogen production, one can claim that biomass is comparatively a better option as it's a renewable source. Normally, biomass is considered neutral in carbon because the carbon released is considered to be equal to the carbon absorbed during the growth of vegatables or wood used in biomass.

The subsequent step in the SMR process is called the water-gas shift reaction. In this step, more hydrogen is produced when carbon monoxide (CO) produced in the above step reacts with steam in the presence of another catalyst. The by-product of this step is carbon dioxide (CO_2).

$CO + H_2O$ –> $CO_2 + H_2$ (+ small amount of heat)

If the greenhouse gas (CO_2) produced in an SMR process is released into the atmosphere, the hydrogen produced would be considered "grey hydrogen" because natural gas was used in this process. If CO_2 was captured and stored (carbon sequestration) then the hydrogen produced would be termed "blue hydrogen." Subsequently, the captured CO_2 can be used in various applications such as oil extraction, building material, food industry, etc.

Hydrogen can be categorized based on the energy sources used for its production.

Green Hydrogen: Produced using clean renewable energy sources. There are no greenhouse gas emissions associated with the production of green hydrogen.

Brown Hydrogen: Produced from coal.

Grey Hydrogen: Produced from natural gas or petroleum.

Blue Hydrogen: Brown or grey hydrogen production combined with carbon capture and storage/sequestration.

Pink Hydrogen: Produced through electrolysis powered by nuclear energy. Sometimes also referred to as purple or red hydrogen.

Yellow Hydrogen: A relatively new category of hydrogen produced through electrolysis using solar power.

HYDROGEN STORAGE:

Although hydrogen has approximately three times the energy content of gasoline or diesel per unit weight, it is nearly 11 times lighter than air. Due to this very low volumetric efficiency of hydrogen, its storage tank for the same amount of energy as offered by other common fuels at room temperature would be disproportionately large. Hence, the density of hydrogen needs to be increased (thus decreasing its volume) in order to store it in a viable-sized storage tank. Also, since hydrogen is highly flammable, its transportation and storage pose additional layers of complexities.

The following hydrogen storage techniques are available.

HIGH-PRESSURE STORAGE OF HYDROGEN IN GASEOUS FORM

Hydrogen is compressed up to 700 bar pressure in the gaseous form. With this method, hydrogen can be stored without lowering its temperature.

STORAGE OF HYDROGEN IN LIQUID FORM

Hydrogen turns into liquid at an extremely low temperature of -423. 17°F (-252.87°C), at the normal atmospheric pressure of 14.69 PSI (1.013 bar). In liquid form, due to its higher density than high-pressure storage in gaseous form, hydrogen offers even higher energy content in a smaller volume. And yes, such a low temperature is required to retain hydrogen in liquid form at atmospheric pressure.

STORAGE OF HYDROGEN IN SOLID FORM

Storage of hydrogen in solid form entails absorption or adsorption of hydrogen by another material. In the previous section, we learned about the basic principles behind various hydrogen production methods and how those methods did (or did not) contribute to greenhouse gas emissions.

Now that we have learned about the fundamentals of hydrogen storage, we will shift our focus to two technologies that use hydrogen to produce electricity, i.e., internal combustion (IC) engine generators and fuel cells.

HYDROGEN IN IC ENGINES:

IC engines can be divided into two categories, compression ignition (CI) engines (e.g.,diesel fueled engines) and spark-ignited (SI) engines (e.g., gasoline, gaseous fueled engines).

Let's understand the impact on the performance and emissions of IC engines when hydrogen is used as a fuel.

EFFECT ON THE IC ENGINE EMISSIONS

IC engines fueled by fossil fuels emit exhaust containing harmful components such as unburnt hydrocarbons (HC), carbon monoxide (CO), oxides of nitrogen (NOx), particulate matter (PM), etc. Conversely, the combustion of pure hydrogen (100% blend of hydrogen) in IC engines produces zero carbon emissions. However, running an IC engine on 100% hydrogen necessitates major design changes.

In the following section we will learn that hydrogen can be blended with a primary fuel as an intermediate solution to minimize the CO, CO_2, HC, and PM emissions. Due to its inherent properties, hydrogen is more suited for use in SI engines than CI engines.

Below are impacts on emission components using hydrogen as a blended fuel source.

Carbon monoxide Emissions

Incomplete combustion of fuel inside IC engines leads to the formation of CO. When hydrogen is blended with traditional fuel, a high 3831°F (2111°C) adiabatic flame temperature of hydrogen raises the temperature of the working fuel and improves the combustion efficiency. In addition, because hydrogen does not have carbon molecules, the result is lower CO and CO_2 emissions.

> Hydrogen burns clean only when combined with pure oxygen. When hydrogen burns with oxygen in the presence of air, other components in the air cause production of oxides of nitrogen (NOx) as by-products harmful to the environement.

EFFECT ON THE IC ENGINE EMISSIONS (CONT.):

Unburned Hydrocarbon (HC) Emissions

Hydrogen does not contain any HC. Therefore, blending hydrogen with traditional fuels and the resulting improved combustion efficiency reduces the amount of unburned HC.

Oxides of Nitrogen (NOx) Emissions

Hydrogen is considered suitable for combustion due to its low ignition energy required and fast flame speed. While its high temperature raises the working fluid temperature, it increases the NOx emissions as well. Therefore, increasing the percentage blend of hydrogen in the fuel results in a further increase in the NOx emissions as well. In addition, the air/fuel ratio, compression ratio, ignition timing, etc. can affect the NOx emissions.

Particulate Matter (PM) Emissions

PM emissions (soot) are observed in diesel-fueled IC engines. Typically the PM emissions level is inversely related to the NOx emissions level.

PM emissions are observed mostly due to the heterogeneous nature of the combustion of diesel fuel.

Adding hydrogen to diesel fuel increases the homogeneity of the flammable mixture and flame speed, which results in a reduced PM level.

EFFECT ON THE IC ENGINE PERFORMANCE

Brake Horsepower (BHP)

The volumetric efficiency (VE) of an IC engine is the actual amount of air flowing through the engine during a combustion process. A VE of 100% means the engine is holding 100% of the air by mass it is theoretically capable of holding. During combustion, hydrogen expands more than other fuels, thus allowing less air in the engine. This results in less VE for hydrogen-powered IC engines, thus reducing their output power (BHP). Therefore, an increase in the percentage of hydrogen blend in the working fuel results in a further decrease in the engine output power (BHP).

Brake Thermal Efficiency (BTE)

BTE is the ratio of the BHP obtained from the engine to the fuel energy supplied to the engine. BTE of IC engines using traditional fuel is 35%–50%. BTE of hydrogen-fueled engines ranges from 20% to 30% depending on the hydrogen blend in the fuel. For example, increasing the hydrogen blend in the fuel from 0% to 50% will decrease the BTE from approximately 30% to 20%.

That means the combustion of hydrogen in IC engines results in less BTE compared to the combustion of traditional fuels. Also, an increased percentage of hydrogen blend in the working fuel results in a further decrease in BTE.

Current research work is focused on developing modern hydrogen-fueled IC engines with BTE higher than 45% and low NOx levels.

HYDROGEN IN FUEL CELLS

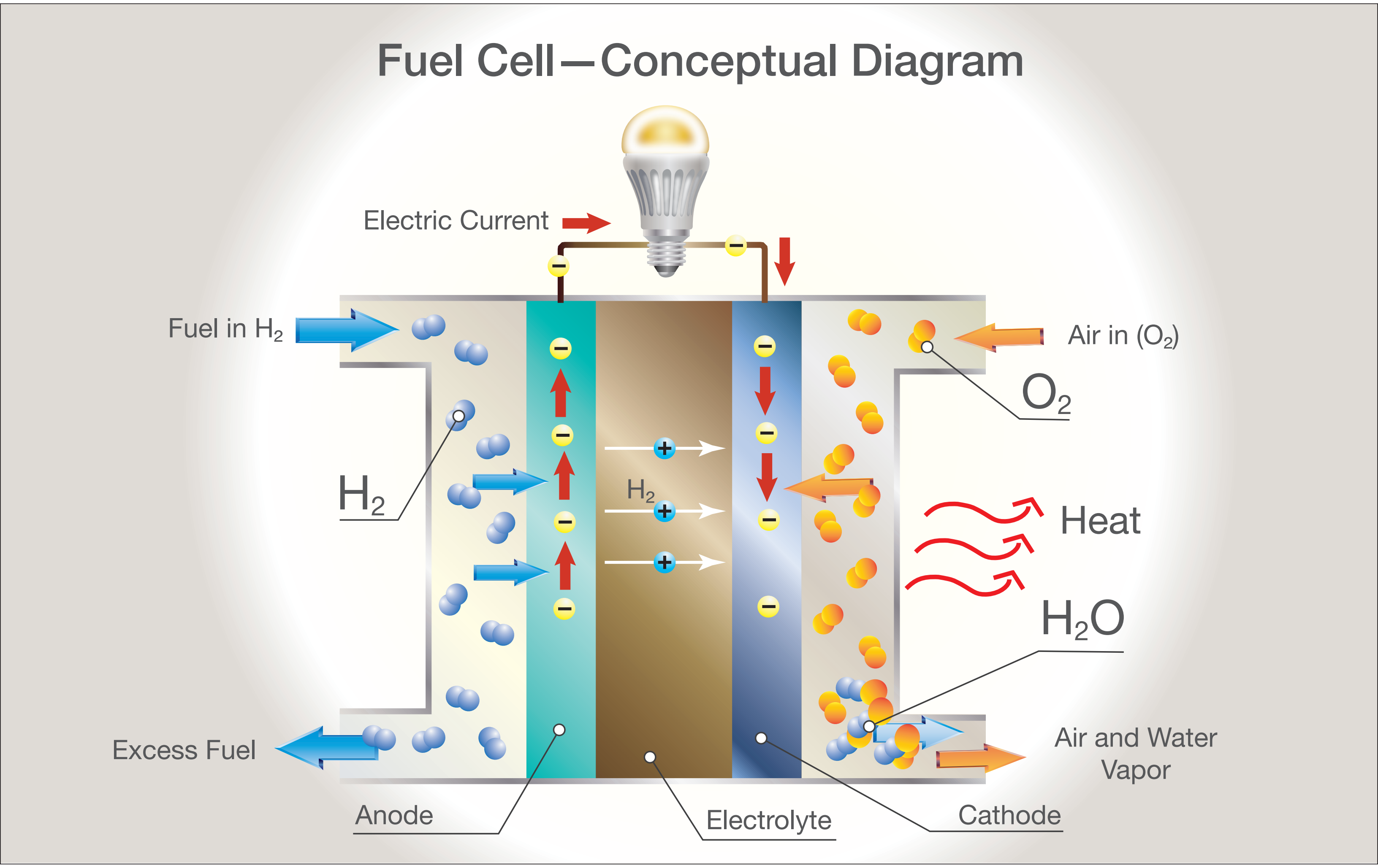
The fuel cell is an electrochemical cell. Simply speaking, it uses hydrogen and oxygen to produce electricity. Conceptually, the principle of operation of a fuel cell is opposite of an electrolytic process. (We learned earlier that in the electrolytic process, electricity is used to split water molecules into hydrogen and oxygen.)

Bear in mind that when pure hydrogen is used in fuel cells, the electricity is produced with only heat and water (water vapor) as by-products. Some types of fuel cells can operate on hydrogen-rich fuel as well. Such fuel cells will have some carbon emissions (depending on the type of fuel used) along with the usual by-products, e.g., heat and water.

Figure 3 is a conceptual diagram of a typical fuel cell. The hydrogen molecules (H_2) enter at the anode and oxygen (O_2) enters at the cathode. The hydrogen atoms in the hydrogen molecules split into electrons and positively charged hydrogen protons.

The electrolyte membrane allows only hydrogen protons to pass through. The electrons are forced through an external circuit, thus generating an electric current. This flow of electrons (electric current) reaches the cathode. There, the negatively charged electrons combine with the positively charged hydrogen protons and oxygen from the air to form water (H_2O). Heat is also dissipated during this process.

Figure 3



HYDROGEN IN FUEL CELLS (CONT.):

A typical fuel cell generates approximately 0.6 to 0.7 volts. The fuel cells are stacked in series to yield the desired output voltage. To produce the desired power output (power = voltage x current), fuel cells are further stacked in parallel to yield the required output current. *Figure 4* below is an image of a typical fuel cell stack.

Fuel cells are classified primarily based on the kind of electrolyte that they use. As a result, different types of fuel cells use different catalysts, operate at different temperature ranges, accept different fuels, etc. These differences play the role in determining the suitability of a particular type of fuel cell for the given application.

At present the following types of fuel cells are being developed or available in the market:

- Polymer Electrolyte Membrane Fuel Cell (PEM)
- Solid Oxide Fuel Cell (SOFC)
- Alkaline Fuel Cells (AFC)
- Phosphoric Acid Fuel Cells (PAFC)
- Molten Carbonate Fuel Cells (MCFC)

Figure 5 on page 9 and *Figure 6* on page 10 summarize the characteristics of each fuel cell technology. Due to wide variability in these characteristics, each fuel cell technology can be suitable for a particular type of application. Some characteristics also support or deter the market adoption of their respective fuel cells.

It would be remiss to not mention hydrotreated vegetable oil (HVO) fuel, which can be a high-quality and sustainable replacement for the ultra-low sulfur diesel fuel, number two currently used in diesel engines.

HVO is produced from renewable resources such as various vegetable oils and animal fat waste streams by hydrogenation using hydrogen and a catalyst at high temperatures and pressures. As HVO is fossil-free, it is commonly referred to as renewable diesel.

A few of the many advantages offered by the HVO fuel are lower NOx and CO_2 emissions, long shelf life of ten years, ability to completely replace fossil diesel without deteriorating the engine performance, and power output. The fact that HVO offers the best coverage among the environmental, operational, and performance parameters without needing engine modifications could significantly accelerate its market adoption.

Be advised hydrogen is required in the process of hydrogenation.

Figure 4

(Reference: https://energy.gov/eere/videos/energy-101-fuel-cell-technology)

Figure 5

Fuel Cell Comparison Chart			
Fuel Cell	**Polymer Electrolyte Membrane (PEM) Fuel Cells**	**Alkaline Fuel Cells (AFC)**	**Phosphoric Acid Fuel Cells (PAFC)**
General Comments	Also called proton exchange membrane (PEM) fuel cell	One of the first fuel cell technologies developed	One of the most mature fuel cell technologies
Basic Technology	• Uses an acid membrane • Uses a solid polymer as an electrolyte and porous carbon electrodes containing a platinum or platinum alloy catalyst	• Uses an alkaline membrane • Uses a solution of potassium hydroxide as an electrolyte	Uses liquid phosphoric acid as an electrolyte and a platinum catalyst on electrodes
Typical Stack Size	1–100 kW	1–100 kW	5–400 kW
Operating Temperatures	Low operating temperature of 80°C.	Low operating temperature of <100°C	Operating temperature: 150–200°C
Start-Up Time	Only a few seconds	Less than a minute.	1–3 hours
Catalysts to Market Adoption	• Electrical efficiency: 45%–65% • Quick response to transient loads • Low operating temperature facilitates better durability • For the same power output, PEM cells are smaller and lighter in comparison with other fuel cells • Due to the above mentioned characteristics and a quick start up time, very promising future in the transportation and electric power generation industries	• Electrical efficiency: 60% • Can use variety of non-precious metals as a catalyst on electrodes	Electrical efficiency: Approximately 85% when used in combined heat and power (CHP) applications
Deterrents to Market Adoption	• Pure hydrogen is needed, which is supplied from external reformers or storage tanks • Low operating temperature leads to expensive catalyst (typically platinum) on electrodes	• Pure hydrogen is needed, which is supplied from external reformers or storage tanks • Highly susceptible to the impurities in the air. Even a small amount of CO2 in the air can adversely affect the fuel cell performance and durability due to carbon formation	• Pure hydrogen is needed, which is supplied from external reformers or storage tanks • When made to produce electricity alone, the efficiency is only 37%–42% which is only slightly better than what's offered by IC engine generators • For the same power output, PAFCs are larger and heavier in comparison with other fuel cells • The platinum catalyst used on electrodes is expensive

Figure 6

Fuel Cell Comparison Chart - Cont.		
Fuel Cell	**Molten Carbonate Fuel Cells (MCFC)**	**Solid Oxide Fuel Cells (SOFC)**
General Comments	Since the commercialization of this technology in the late 1990s, it has progressed steadily with improved performance	The key to accelerate the market adoption of this technology is to develop a highly durable material (at low cost) that will withstand 1000°C operating temperature of the SOFC
Basic Technology	• Uses molten carbonate salt mixture as an electrolyte. It is suspended in a porous and chemically inert ceramic lithium aluminum oxide matrix • At the high operating temperature of 600°–700°C at which MCFCs operate, methane and other light hydrocarbons in these fuels are converted to hydrogen within the fuel cell itself by a process called internal reforming	• Uses a hard, non-porous ceramic compound as an electrolyte • At the high operating temperature of 1000° C at which SOFCs operate, methane and other light hydrocarbons in these fuels are converted to hydrogen within the fuel cell itself by a process called internal reforming
Typical Stack Size	300 kW–3 MW	1 kW–2 MW
Operating Temperatures	High operating temperature: 600°–700°C	Very high operating temperature up to 1000°C
Start Up Time	A few minutes.	Several minutes to an hour
Catalysts to its Market Adoption	• Electrical efficiency: 50% • Offers an electrical efficiency of more than 85% when used in combined heat and power (CHP) applications • Due to the high operating temperature, non-precious metals can be used as catalysts on electrodes, thus reducing the cost • The internal reforming process negates the need for an external reformer, thus reducing the cost • The internal reforming ability allowed variety of hydrogen rich fuels such as natural gas, biogas etc.	• Electrical efficiency: 60% • Offers an electrical efficiency up to 85% when used in combined heat and power (CHP) applications. • Due to the high operating temperature, non-precious metals can be used as catalysts on electrodes, thus reducing the cost • The internal reforming process negates the need for an external reformer, thus reducing the cost. • The internal reforming ability allows variety of hydrogen rich fuels such as natural gas, bio-gas, etc.
Deterrents to Market Adoption	• High operating temperature - Adversely affects the fuel cell durability - Leads to a long start up time Hydrogen-rich fuels tend to leave carbon footprint	• High operating temperature - Requires thermal shielding to retain heat and protect personnel - Adversely affects the fuel cell durability - Leads to a long start up time (minutes to hours) • Hydrogen-rich fuels tend to leave carbon footprint

CONCLUSION:

Hydrogen is stable only in its molecular form. It is abundantly available in various compounds found on Earth, and energy must be spent to extract hydrogen. The production of energy utilized in hydrogen production or the hydrogen production itself may produce greenhouse gases.

We discussed the fundamentals of using hydrogen in IC engines and fuel cells for electric power generation.

Increasing hydrogen blend in the traditional fuel in IC engines does lower HC, CO, and PM emissions. But these benefits come at the cost of increased NOx emissions and diminished engine performance and power output. The combustion of pure hydrogen (100% hydrogen) in IC engines leads to carbon-free emissions. However, running an IC engine on pure hydrogen would entail major design changes and power derate in the engine.

Fuel cells are more energy-efficient than combustion engines. Various types of fuel cells are available in the market to serve varied application needs. Fuel cell technology has been the focus of research and development in the energy sector with a lot of promising advancements being made in the electric power generation and transportation industries.

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