

Fuel Cell Based Automobile Engines

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Abstract: *There is a serious problem of the depleting oil reserves throughout the world and demand and dependence on the conventional oil based vehicles. Petroleum based vehicles are one of the major contributor to the environmental pollution. So there is an immense need for the automobile industry to shift from the conventional ways to newer and environmental friendly ways.*

Keywords: Fuel cell, Eco friendly, automobile

1. Introduction of Fuel Cell

A fuel cell is a technology which utilizes the process of production of electrical energy from chemical energy. It uses a fuel source and oxygen gas.

Operations in fuel cell

The fuel cell consists of three parts- cathode, anode and electrolyte. The fuel comes from the anode side while oxygen comes from the cathode side. The fuel that came from the anode is now broken into negatively charged electrons and positively charged ions; this process is assisted by the catalyst present at the anode. The ions then come into the electrolyte; the electrolyte only allows the positive ions to pass through it so the electrons are forced to travel in the outer circuit from anode to cathode. Current is created by the electrons travelling through the outer circuit and the positive ions travelling through the electrolyte, when they reach the cathode. The electrons and the positive ions interact at the cathode with the oxygen and reacts to form a product, a byproduct in this process. The byproduct is water in the case of hydrogen fuel cell.

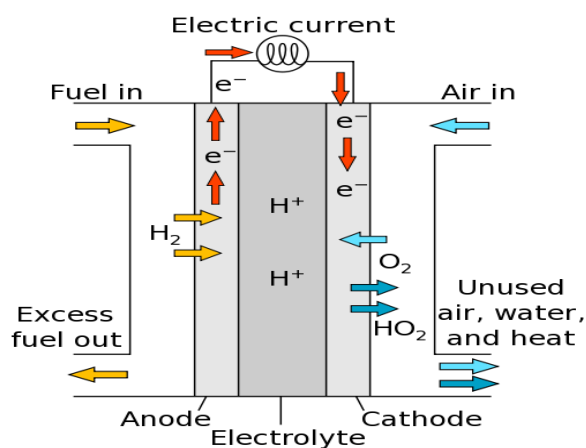


Diagram of Fuel Cell Operation
(Source: Wikimedia Commons)

Types of fuel cell

Fuel cells are of various types, they are mostly characterized on the basis of the electrolytes they use. The change of electrolytes changes the whole working mechanism of the cell, the electrochemical processes changes due to the effect of catalysts, the transport of the charged ions, the temperature range in which the reaction occurs, fuel used and other factors. Many types of fuel cell are currently under development. Different fuel cells are used for different applications on the basis of their potential development,

temperature scale, by product etc. Here are some of the most famous fuel cells:



1) Polymer electrolyte membrane fuel cells (PEM)

They are also known as proton exchange membrane fuel cell. It uses only hydrogen, oxygen and water. In this process pure hydrogen is used directly from tanks and oxygen from the atmosphere is used. The PEM cells produce high power density. They have light weight and low volume. They use porous carbon electrodes and platinum or its alloy catalyst.

These are mainly used for transport applications and some stationary applications. PEM fuel cells are mostly used in automobiles like car and busses, majorly due to its fast startup time and efficient power to weight ratio.

2) Reversible fuel cells

These fuel cell systems use electricity from solar power, wind power and others to exploit the method of electrolysis in which water is broken into hydrogen and oxygen. This also uses hydrogen and oxygen to produce electricity and also produces water and heat as byproduct. This technology is capable enough to provide power at the time of need, but at times in most favorable conditions it produces extra energy, which needs to be stored in the form of hydrogen. This energy storage capability of these cells can be a milestone for renewable methods of energy production.

3) Direct methanol fuel cells:

Unlike the most of the fuel cells which uses hydrogen directly in gaseous form or which uses hydrogen by extracting it from hydrogen rich fuel sources like methanol, ethanol or other hydrocarbon fuel, direct methanol fuel cells uses pure methanol at the anode for powering the system. Methanol has a higher energy density than hydrogen fuel, so

unlike the hydrogen fuel cells, it doesn't need stacking. But if compared to petroleum or gasoline it has a lower energy density. Methanol is also very economical and easier to transport using the available transportation system which well established for liquid state transportation.

4) Alkaline fuel cells

These fuel cells are composed of electrolytes of potassium hydroxide solution in water and consist of non-precious metals as catalyst. Their alkaline membrane sets them apart from PEM fuel which has acid membrane. They have efficiency above 60% due to tremendous rate of electrochemical reactions that take place in it. Even though alkaline membranes have lower susceptibility of CO₂, prolonged exposure to CO₂ can have drastic effect on its performance due to formation of a layer of carbonate.

5) Phosphoric acid fuel cells

This fuel cell consists of liquid phosphorus as electrolyte, carbon electrode containing platinum catalyst and Teflon bonded silicon based matrix. It is primarily used for stationary power generation. These cells are susceptible to exposure to carbon monoxide as carbon monoxide binds to the platinum catalyst at the anode. They are more efficient for generation of heat and electricity together (85%) rather than generation of only electricity (37-42%). They are less powerful as compared to other fuel cells of the same dimensions. Since it uses expensive platinum catalyst as a result they are quite expensive.

6) Molten carbonate fuel cells

The electrode consists of molten carbonate salt mixture suspended in lithium aluminium oxide matrix. These cells are specially designed to work at a high temperature range (around 650C). Due to this, non-precious metals are used as a catalyst. An efficiency of 65% is achieved when molten carbonate is combined with turbine. At higher temperature where these cells primarily work, methane and other hydrocarbons which are already present in the fuel are converted into hydrogen through internal reforming. As a result there is no requirement of an external reformer, thus it is cost effective.

7) Solid oxide fuel cells

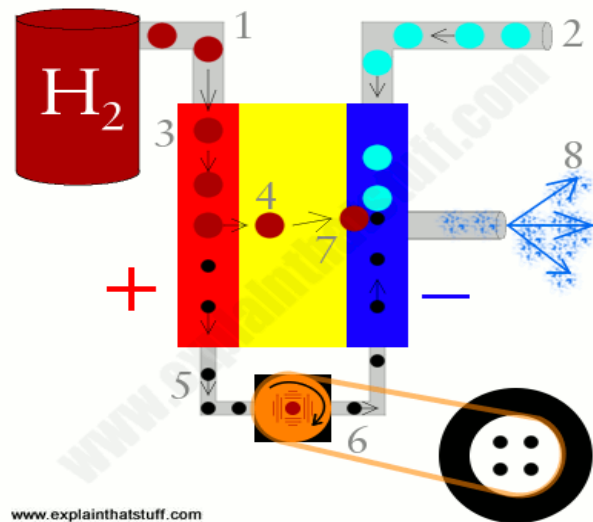
They use non ceramic compounds as electrolyte. They also operate at a very high temperature like molten carbonate fuel cells; as a result it does not use precious metal as a catalyst, thereby reducing the cost. Also, internal reforming takes places which further adds to cost reduction. These cells are sulphur resistant and cannot be poisoned by carbon monoxide. The high temperature serves as a disadvantage as these fuel cells requires significant time to start up. It also requires a lot of thermal shielding to retain heat.

2. Production of electricity in fuel cells

Fuel cell produce electricity by electrochemical reaction. It is a chemical reaction in which due to electron transfer electricity is produced. Fuel cell has four parts – anode, cathode, electrolyte and electric circuit.

- 1) **Anode**- made of platinum.
- 2) **Cathode**- reaction occurs at the cathode when the ions interact with the fuel introduced.
- 3) **Electrolyte**- made of special polymer and protons can pass through it only because if free electrons and other material pass through it and disturb the chemical reaction which will affect the efficiency.
- 4) **Electric circuit**- in which part (here automobile engine) we want to use electricity we will connect that in series with this circuit.

In the given fuel cell hydrogen gas tank is joined at cathode and oxygen gas (from air) reach at cathode.



At anode hydrogen gas convert in H⁺ ions in the presence of catalyst



These protons (H⁺) pass through electrolyte circuit and reach at cathode, while free electrons can't pass through electrolyte so they pass through electric circuit with some velocity so they produce electricity in this circuit.

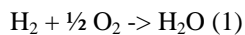
When these electron reach at cathode then O₂ gas in the presence of catalyst gain these electron and convert in O²⁻ ions. These O²⁻ react with H⁺ ions and produce water. We will remove this water to keep dry the fuel cell. Produced water is pure we can use it for drinking and other purpose.

This is PEM fuel cell, which keeps running if we supply continuously Hydrogen and Oxygen gases. Here Hydrogen is limiting reagent because we supply Oxygen from air. Hydrogen catch fire very fast and is very explosive so we should keep it in strong tanks(titanium or other strong material).

3. Thermodynamics of Fuel Cell

To explain functioning of fuel cell systems we use the approach of energy balance. In fuel cells energy balance description is based on energy conversion processes – power generation, heat loss, electrochemical reactions etc. Energy balance description is different for various fuel cells because in every fuel cell different kinds of electrochemical reaction happen. The fuel cell reaction can be divided into two half-

cell reactions. In case of hydrogen fuel cell simplest chemical reaction can be represented as



From thermodynamic point of view –Maximum work output = Change in free energy of above reaction

Here we take Gibbs free energy into account not the Helmholtz free energy because it is more practical to carry a chemical reaction at constant temperature and pressure rather than constant temperature and volume.

In the above reaction –

ΔG = Gibbs free energy of products – Gibbs free energy of reactants = - Ve

So this is a spontaneous and thermodynamically accessible reaction.

We can represent Gibbs free energy as

$$\Delta G = -nFE$$

Here, n = number of moles of e⁻ transferred in reaction

F = Faraday constant

E = reversible reduction cell potential

In case of standard conditions –

$$\Delta G^0 = -nFE^0$$

E⁰ = standard cell potential

For given reaction (1)

$$n = 2, \Delta G = -229 \text{ KJ/mol}, F = 96500 \text{ C/g. mole e}^-$$

So,

$$E = -\Delta G/nF = 1.229 \text{ Volt.}$$

ΔH for a fuel cell reaction

= (total energy of products – total energy of reactants) at constant pressure

= heat released at constant pressure

We can also define

$$\Delta H = -nFE_t$$

E_t = thermo neutral potential

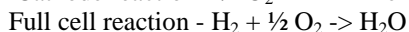
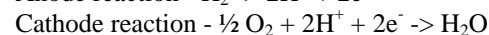
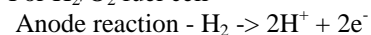
For given reaction (1)

$$E_t = 1.48 \text{ Volt}$$

Fuel cells performance can be determined by electrochemical reactions that are different in various fuel cells. Also the favorable conditions will be different for every fuel cell reaction. For example – temperature, pressure. As we increase temperature reactions will shift forward and backward according to le chatelier principle. Low temperature fuel cells (polymer electrolyte fuel cells or H₂/O₂ fuel cell) require noble metal (platinum, gold) electrolysis both at anode and cathode for a good rate of reaction.

In case of low temperature fuel cell Carbon monoxide (CO) poisons to noble metal electrolysis.

For H₂/O₂ fuel cell –



Here n = 2

Nernst equation for this cell reaction –

$$E = E^0 + \frac{RT}{2F} \ln\left(\frac{P_{\text{H}_2} * P_{\text{O}_2}^{1/2}}{P_{\text{H}_2\text{O}}}\right)$$

$$= E^0 + \frac{RT}{2F} \ln\left(\frac{P_{\text{H}_2}}{P_{\text{H}_2\text{O}}}\right) + \frac{RT}{2F} \ln\left(P_{\text{O}_2}^{1/2}\right)$$

Here,

E⁰ = standard reduction cell potential

E = equilibrium reduction cell potential

P_{H₂} = pressure of H₂ gas

P_{O₂} = pressure of O₂ gas

P_{H₂O} = pressure of water or steam

Instead of H₂ if we use Hydrogen carbonates than at anode we will get CO₂ as by product.

Ideal standard potential for H₂/O₂ fuel cell –

$$E^0 = 1.229 \text{ Volt (if H}_2\text{O is liquid product)}$$

$$E^0 = 1.18 \text{ Volt (if H}_2\text{O in gaseous state)}$$

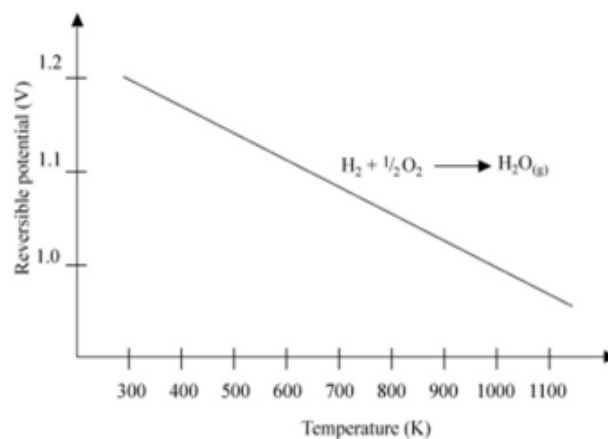
We can understand this difference in E⁰ due to different enthalpy change in both cases. If H₂O is gaseous state than magnitude of enthalpy change is less than cell reaction compared to when H₂O is in liquid state. So E⁰ is less in case of gaseous water.

As we know,

$$\Delta G = -RT \ln(k)$$

So we can say that as temperature increases ΔG will decrease for this reaction.

Variation of standard fuel cell potential with temperature is below –



So we can see that high temperature fuel cells are effectively affected by temperature.

Ideal and actual fuel cell responses can be represented as below given diagram.

Actual cell potential is always less than ideal cell potential because of irreversible losses in actual fuel cells. There are different kind of polarizations are represented in this diagram which are responsible for these losses.

The activation polarization is the major in all of these which happens in low current region.

$$\eta_{\text{act}} = \frac{RT}{\alpha nF} \ln(i/i^0)$$

here, η_{act} = activation polarization

α = charge transfer coefficient

i = current density

i⁰ = exchange current density

The reason for activation polarization is slow electrochemical reaction at electrode surface. Ohmic polarization happens from resistance in flow of ions in the electrolyte and flow of electrons from one electrode to other through electric circuit.

$$\eta_{\text{ohm}} = iR_c$$

η_{ohm} = ohmic polarization

R_c = cell resistance

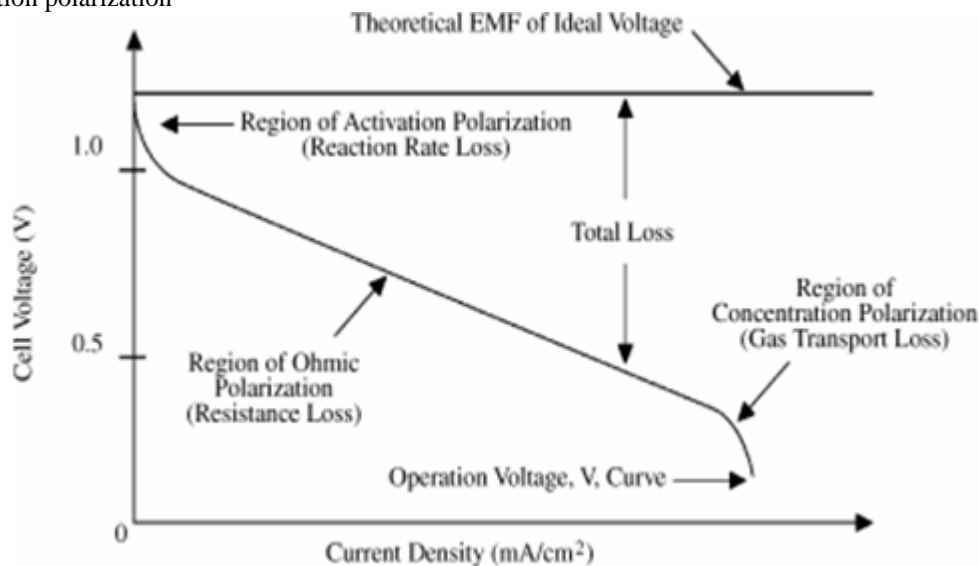
It can be reduced by increasing ionic conductivity of electrolyte and electrode separation. Concentration Polarization happens due to variation in current density.

$$\eta_{\text{con}} = (RT/nF)\ln(1-i/i_L)$$

η_{con} = Concentration polarization

i_L = limiting current density

It happens due to slow diffusion of gases in electrode pores, reactants solution in electrolyte, diffusion of reactants and products from reactant sites etc.



Thermodynamic principles

The effect of temperature and pressure and temperature on Gibbs free energy can be shown as-

$$(\partial E/\partial T)_P = \Delta S/nF$$

$$(\partial E/\partial P)_T = -\Delta V/nF$$

ΔV = change in volume

ΔS = change in entropy

E = cell potential

We know H_2/O_2 fuel cell entropy change is negative for increase in temperature. From above equation cell potential will also decrease in increase in temperature.

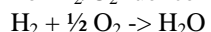
Here volume change is negative. So cell potential will increase with increase in pressure. Normally fuel cells operates at cell potential cell than reversible cell potential due to internal resistance.

Efficiency of fuel cell

Efficiency η_e = useful output energy / ΔH

Ideal efficiency = $\Delta G/\Delta H$

For H_2/O_2 fuel cell



$$\Delta G^0 = G_{H_2O}^0 - G_{H_2}^0 - G_{O_2}^0/2$$

Here $\Delta G^0 = 237.1$ KJ/mole

$\Delta H^0 = 285.8$ KJ/mole

$$\text{So ideal efficiency at standard condition for cell} = \Delta G^0/\Delta H^0 = 237.1/285.8 = 0.83$$

This efficiency can be represented in term of the ratio of actual operation voltage and ideal voltage

η_e = useful output energy / ΔH

= useful output power/($\Delta G/0.83$)

$$= V_{\text{cell}}I/(V_{\text{ideal}}I/0.83) = 0.83V_{\text{cell}}/V_{\text{ideal}}$$

For this fuel cell we $V_{\text{ideal}} = 1.229$ Volt

$$\text{So } \eta_e = 0.83V_{\text{cell}}/1.229 = 0.675 V_{\text{cell}}$$

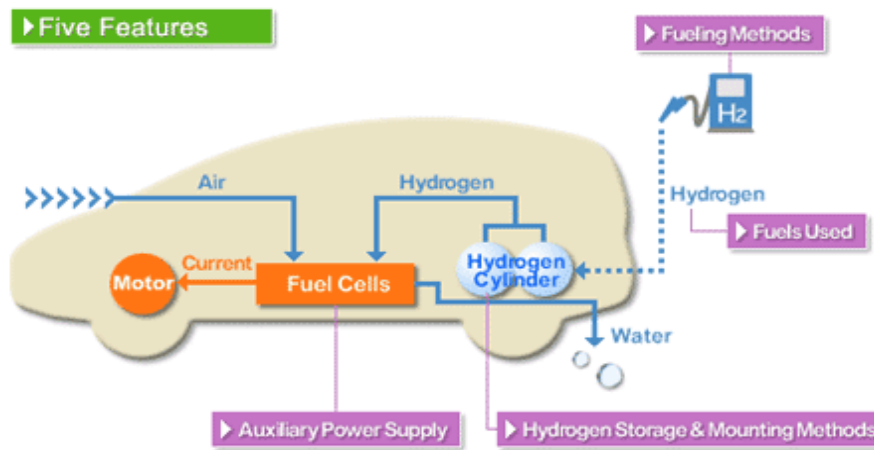
If we increase the current density that will increase the cell actual voltage. So from efficiency equation due to increase in actual cell voltage efficiency will also increase.

We cannot reach at efficiency of 1 because it is impossible to get ideal condition accurately. But by decreasing the internal resistance we can increase the efficiency.

Fuel cells in Automobiles

There is a serious problem of the depleting oil reserves throughout the world and demand and dependence on the conventional oil based vehicles. Petroleum based vehicles are one of the major contributor to the environmental pollution. So there is an immense need for the automobile industry to shift from the conventional ways to newer and environmental friendly ways. We have to develop a vehicle that utilizes cleaner fuels. The most efficient and popular alternative fuel vehicles that came up is the battery electric vehicle (BEV). BEVs have already got a success on the road, many companies has launched its electric car model like Leaf from Nissan, Tesla Model S, BMW i3 etc. Cars of this type carries a large battery, the battery drives an electric motor which propels the vehicle.

The hydrogen fuel cell vehicle (HFCV) is the other idea booming in this industry. This technology, like the BEVs also propel on motors, the difference is that these use fuel cells to generate the required electricity by utilizing compressed hydrogen gas instead of heavy batteries. For this technology to be effective we require many fuel cells to be connected to each other because the energy produced by single fuel cell is less, and will not be able to propel the vehicle. This connection of the fuel cell is called stacking.



An ideal fuel cell vehicle model (<http://www.jari.or.jp>)

4. Advantages over other Automobile Engines

Fuel cells have various advantages as compared to conventional power sources like combustion engines or batteries.

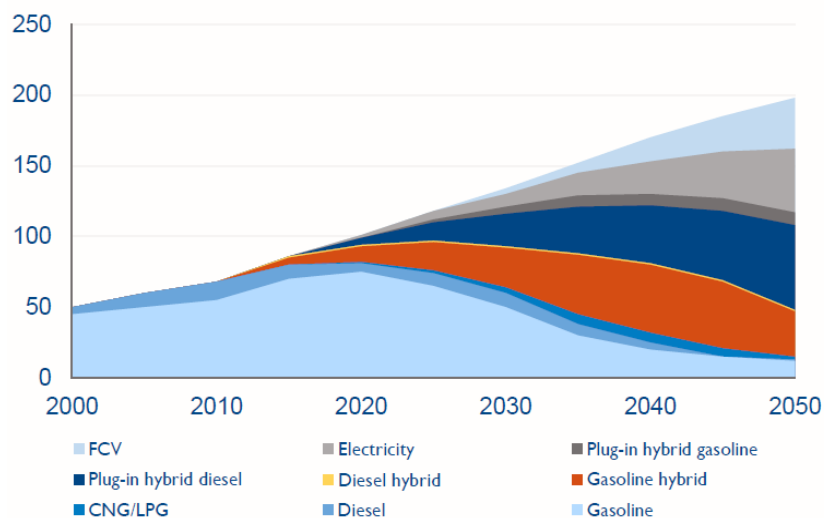
Benefits include:

- 1) The efficiency of a fuel cell is much higher than a diesel or gas engine.
- 2) Refueling Time: A few minutes while electric vehicles take much higher time to charge a battery.
- 3) Most fuel cells do not produce sound while working hence has an edge over combustion engines.
- 4) Fuel cells can eliminate pollution caused by burning fossil fuels; for hydrogen fuelled fuel cells, the only byproduct is water.
- 5) If we produce hydrogen from electrolysis of water by harnessing renewable sources of energy, then using fuel cells eliminates greenhouse gases over the whole cycle.
- 6) Fuel cells do not depend on fuels such as oil or gas and can, therefore, reduce economic dependence of a nation on oil producing countries.
- 7) Since hydrogen can be produced anywhere where there are water and a source of power, therefore it does not require long supply chains.
- 8) Fuel cells do not have any "memory effect" when they are getting refueled, while batteries do have.
- 9) Maintenance of fuel cell is less due to a few moving parts only.
- 10) Weight and volume of energy storage – Compared to EV batteries, H2 requires less weight and volume for energy storage to enable the same distance range: a lithium-ion battery system requires about six times more weight and twice the volume to allow comparable driving ranges

5. Market and Future of Fuel Cell Automobiles

Fuel Cell Vehicles market are expected to grow significantly, but it will take some more time. The International Energy Agency (IEA) estimates fuel cell vehicle market share of about 17% by 2050. (35 million annual unit sales).

FCV sales volume predictions based on long-term powertrain mix scenario (Mln units)



Source: International Energy Agency 2012 (IEA)

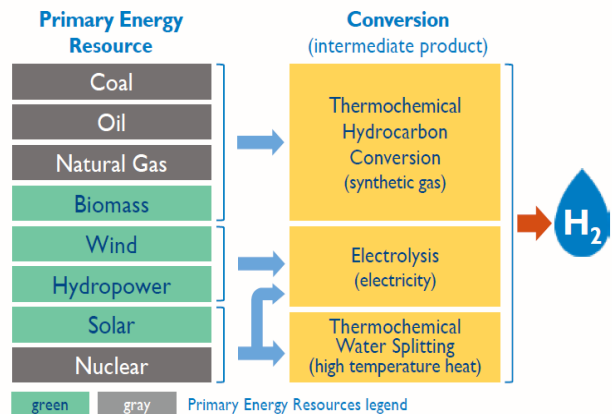
Slow penetration of Fuel Cell Vehicle is due to:

- 1) Cost of Vehicles: The high cost of FCV's is due to the use of expensive catalysts and materials like platinum and no mass production.
- 2) Distribution infrastructure: FCV's require an entirely new and expensive infrastructure system for each step of the chain, from hydrogen transport through storage and delivery to the vehicle.
- 3) Hydrogen production: For FCVs to be competitive in terms of Greenhouse Gases - reduction, the right decisions to achieve a low-cost and low-GHG production methods need to be pursued.

Hydrogen can be harnessed from various resources similar to electricity, each having a different impact on the greenhouse gases footprint.

In terms of GHG-footprint, it is more favorable to produce hydrogen from renewable primary energy resources (green) rather than gray.

Hydrogen production primary energy resources and intermediate products



Source: Arthur D. Little analysis; The Hydrogen Transition, Joan Ogden, Christopher Yang, Michael Nicholas, and Lew Fulton (2014)

Comparison of alternative and traditional fuel vehicles

	Best Option Worst Option			Traditional
	FCVs	BEVs	PHEVs	
Refueling Time	Few minutes	>1 hour	Few minutes/ >1 hour for electric recharge	Few minutes
Drive Range	>450 km	400km (by 2018-2020)	Comparable to ICE	Up to more than 1000 km
Price of Car	Additional cost compared to BEV (BEV + FC system)	Additional cost compared to ICE	Additional cost compared to ICE	Lower benchmark (consolidated technology)
Fuel Efficiency	Higher than ICE but lower than BEVs	Higher than ICE and FCVs	Higher than ICE but lower than BEVs	Lower benchmark
Fueling Infrastructure	H ₂ stations similar to gas stations	Chargers (home and public)	Chargers / Gas stations	Gas stations

* But with a lower power battery

Source: Arthur D. Little analysis

6. Limitations of Fuel Cell Vehicles

- 1) Leads to the emission of Nitrogen Dioxide which is a toxic gas and can be harmful when ingested by humans. It can cause problems like lung edema etc.
- 2) Transportation of hydrogen is expensive.
- 3) Hydrogen takes a lot of time to break its element and thus make the cost of process higher.
- 4) Hydrogen is colorless and odorless, therefore can be inhaled or ingested is possible without being noticed, which can lead to asphyxiation.
- 5) In case of fire, hydrogen flames are invisible in the daytime, making it dangerous for firefighters.
- 6) Suitable reliability and durability must be achieved. The performance of every fuel cell gradually degrades with time due to a variety of phenomena. The automotive fuel cell must withstand load cycling and freeze-thaw

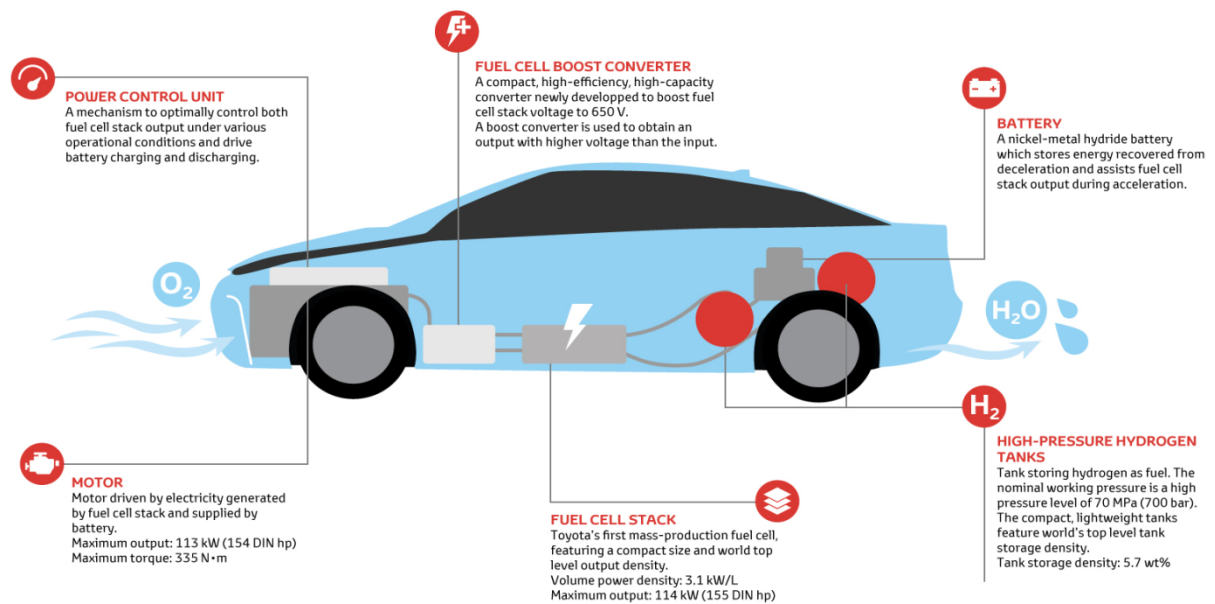
environmental swings with an acceptable level of degradation from the beginning-of-lifetime.

- 7) Sensors and online control systems for fuel cell systems are needed, especially for the transient operation, where performance instability can become a major issue.

7. Fuel cell vehicle in news

The Toyota Mirai is a hydrogen fuel cell electric vehicle (FCEV), which makes it a rare breed anywhere in the world. Mirai is the new sensation in the automobile industry, it has all that makes it the centre of attraction, be it its design, its technology, the class and everything we can think of. Hyundai and Audi also have a deal to collectively work on development of fuel cell car. Mercedes is also in the race.

Fuel cell electric technology explained

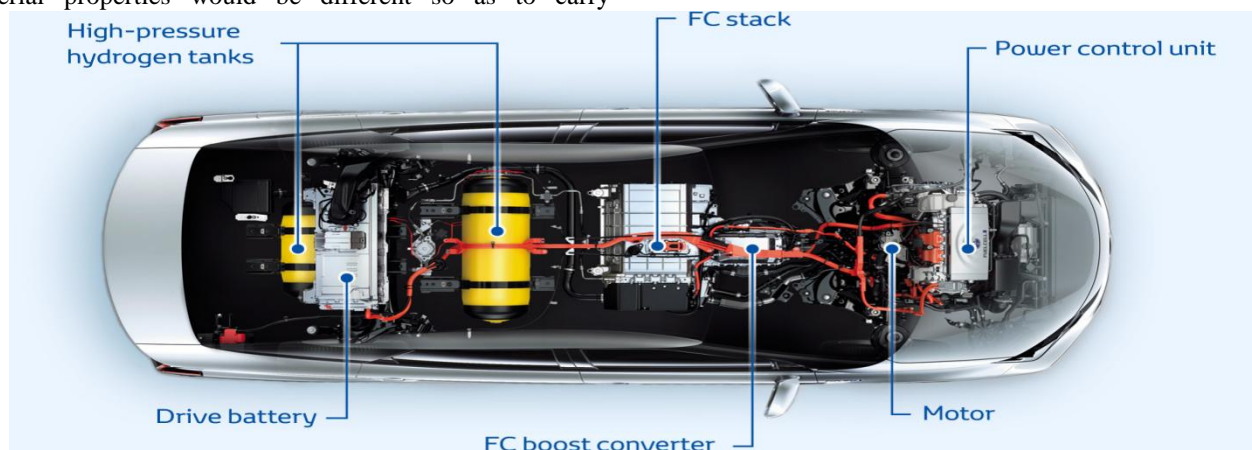


Toyota Mirai mechanism

Here is what Toyota motors say about Mirai:

Toyota says that the fuel filling system of this vehicle will be similar to any other vehicle, the car would have a fuel tank like the normal petrol one in appearance, but the material properties would be different so as to carry

compressed hydrogen. This can run the same distance on filling the tank full of hydrogen as that of a similar size of tank full of petrol. The drive will be smooth and quite. The built body of the car is strong. There are no other harmful emissions but water vapour.



8. Conclusion

Fuel Cell Vehicle is the future of the automobile industry. As we saw there are very few limitations/disadvantages. And all the disadvantages we talked are not acting as limitations since new technologies are built day by day. Most of the companies today are investing in R&D of Fuel Cell Automobiles. Even in the coming years, hydrogen vehicle will be more successful than an electric vehicle.

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