FUEL-CELL: POWER FOR FUTURE

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Abstract. Although fuel-cell was invented in 1830, its intensive development took place in the last decades of XX century. Theoretical background of fuel-cell operation have been given. Application of fuel-cell to automotive vehicles as a prime mover and as auxiliary energy source have been shown. Three main types of fuel-cell: hydrogen, methanol and gasoline are discussed. Forecast of application of fuel-cell to automotive vehicles are presented.

1. Introduction

In the beginning of 19^{th} century, simultaneously with creation of theoretical base of heat engines (Nicolas Carnot, 1798-1832), physicists and chemists looked for a direct way of conversion of fuel energy into electrical energy without need for transfer it into heat. With development of electro-chemistry, chemical battery was invented (Robert Bunsen, 1811-1899), in which chemical energy is converted into electric current due to non-reversible chemical reaction, until the potential energy of "a fuel" is exhausted. There was need however to have a cell in which electric energy would be gained as long as fuel energy was supplied to it. In 1830 sir William Grove experimentally showed, that electrolysis of water is reversible process and H_2 and O_2 could be produced in electrochemical cell (fuel cell), but the state of science and technology was insufficient to build fuel-cell then, and the idea was left behind for one hundred years. Development of chemical physics, especially the work of van't Hoff (Jacobus van't Hoff, 1852-1911) on reversible isotermal reactions (van't Hoff box) created a base on which Francis Bacon in 1930s built electrochemical cell (work was interrupted by II World War) and in 1959 developed 6 kW hydrogen – oxygen fuel-cell [1]. This gave rise to R&D work on fuel-cell at the end of the last century.

2. Theoretical Background

2.1. Van't Hoff equilibrium box

Chemical equilibrium can by best illustrated by the use of van't Hoff equilibrium box (Fig.1) in which reversible chemical isobaric-isothermal reaction:

$$2H_2 + O_2 \longleftrightarrow 2H_2O \qquad (1)$$

(In general case: $aA + bB \rightarrow mM + nN$)

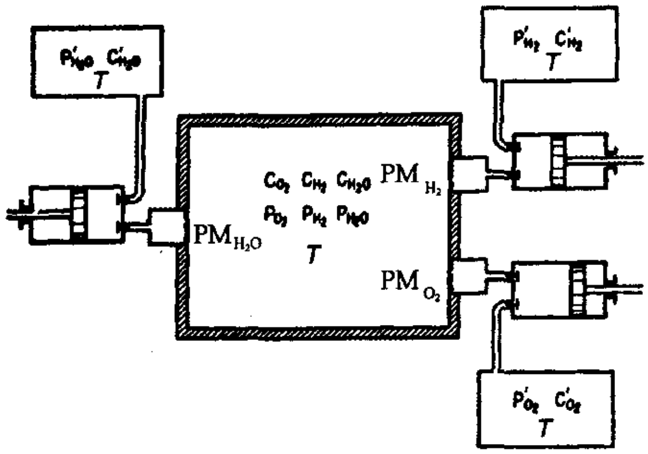

Fig.1. Van't Hoff H_2-O_2 equilibrium box
PM_s – permeable membrane only for species s

is in equilibrium state (Fig.2).

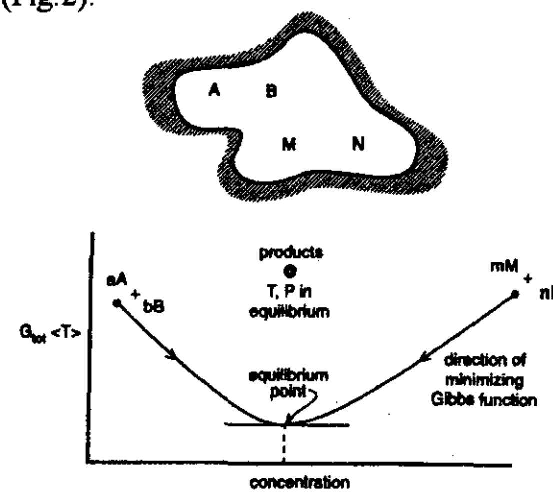

Fig.2. Equillibrium of reaction: $\nu_A A + \nu_B B \leftrightarrow \nu_M M + \nu_N N$ [1]

Any energy transfer to the box or from the box results in change of mixture composition, pressure, temperature and a new equilibrium state. When species A and B are supplied to the box (through permeable only for A and B membranes respectively) in a proper rate ratio and M and N removed (also through permeabrane only for M and N membranes respectively), under the condition that reaction (1) between A and B is electrochemical, electric energy can be removed from the box and then the box is called fuel-cell, Fig.3.

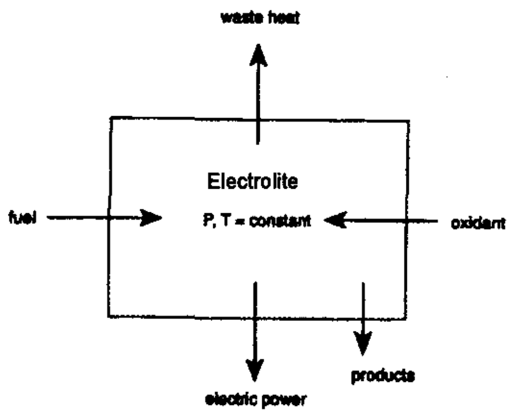

Fig.3. Fuel-cell schematic

2.2. How fuel-cell acts

Fuel-cell is van't Hoff box, in which take place controlled isobaric-isothermal reversible oxidation electrochemical reaction. Scheme of fuel-cell is shown in Fig.4 on example of hydrogen-oxygen fuel-cell.

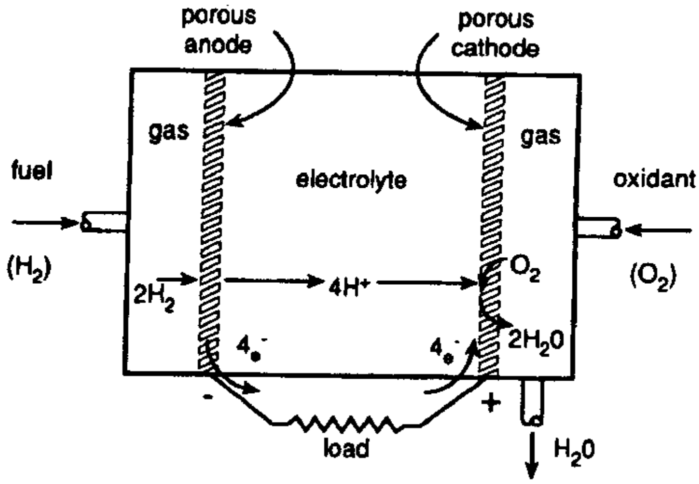

Fig.4. Hydrogen fuel-cel [1]

A fuel-cell consists of an porus anode supplied by a gaseous fuel (hydrogen) and a cathode supplied by an oxidant (usually air), separated by the proton exchange membrane (PEM), the solid polymer (SPFC) or any other – Table 1.

Table 1. Main fuel cell classifications [2]

Type	Electrolyte	Operating temp (°C)	Principal applications
PEMFC	Poly-perfluoro sulfinic acid	25-105	Transport
DMFC	Poly-perfluoro sulfinic acid	70-105	Transport
SOFC	Zirconium & yttrium oxides	750-1000	Transport, power generation
AFC	Potassium hydroxide	50-200	Space, transport
MCFC	Lithium and potassium carbonates	630-700	Power generation
PAFC	Phosphoric acid	180-210	Power generation
Key: SPFC – solid polymer fuel cell; SOFC – solid oxide fuel cell; AFC – alkaline fuel cell; PEMFC – proton exchange membrane; MCFC – molten carbonate fuel cell; DMFC – direct methanol fuel cell; PAFC – phosphoric acid fuel cell			

Hydrogen at an anode dissociates into hydrogen cations and electrons:

$$2H_2 \rightarrow 4H^+ + 4e^-$$

Hydrogen ions travel through electrolyte to cathode, while the electrons flow around the external circut also to the cathode. At cathode, the oxygen accepts the electrons to form oxide ions and afterwards reacts with hydrogen ions to form water which is only wast by-product.

$$4H_2 + 4e^- + O_2 \rightarrow 2H_2O$$

Other ideal fuel-cell reaction and theoretical efficiency are shown in Table 2.

Table 2. Fuels, chemical reactions and theoretical efficiency of fuel – cells [1]

„Fuel"	Reactions	Theoretical Efficiency [%]
Hydrazine (aq)	$N_2H_4(aq) + 4OH^- \leftrightarrow N_2 + 4H_2O + 4\bar{e}$ $N_2H_4(aq) + O_2 \leftrightarrow N_2 + 2H_2O$	99.4
Ethanol (aq)	$C_2H_5OH(aq) + 3H_2O \leftrightarrow 2CO_2 + 12H^+ + 12\bar{e}$ $C_2H_5OH(aq) + 3O_2 \leftrightarrow 2CO_2 + 3H_2O$	97.5
Methanol (aq)	$CH_3OH(aq) + H_2O \leftrightarrow CO_2 + 6H^+ + 6\bar{e}$ $CH_3OH(aq) + \frac{3}{2}O_2 \leftrightarrow CO_2 + 2H_2O$	97.1
Benzene	$C_6H_6 + 12H_2O \leftrightarrow 6CO_2 + 30H^+ + 30\bar{e}$ $C_6H_6 + \frac{15}{2}O_2 \leftrightarrow 6CO_2 + 3H_2O$	97.2
Propane	$C_3H_8 + 6H_2O \leftrightarrow 3CO_2 + 20H^+ + 20\bar{e}$ $C_3H_8 + 5O_2 \leftrightarrow 3CO_2 + 4H_2O$	95.0
Ethane	$C_2H_4 + 4H_2O \leftrightarrow 2CO_2 + 12H^+ + 12\bar{e}$ $C_2H_4 + 3O_2 \leftrightarrow 2CO_2 + 2H_2O$	94.3
Methane	$CH_4 + 2H_2O \leftrightarrow CO_2 + 8H^+ + 8\bar{e}$ $CH_4 + O_2 \leftrightarrow CO_2 + 2H_2O$	91.9
Hydrogen	$H_2 \leftrightarrow 2H^+ + 2\bar{e}$ $H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O$	83.0

Hydrogen fuel-cell operates at typical temperature 90°C and produces maximum theoretical voltage of 1,23 V, but operates at 0,6-0,8 V. For most applications the cells are combined in series to form a stack in order to cummulate voltage and power.

Current-voltage characteristics of hydrogen-oxygen fuel-cell is shown in Fig.5.

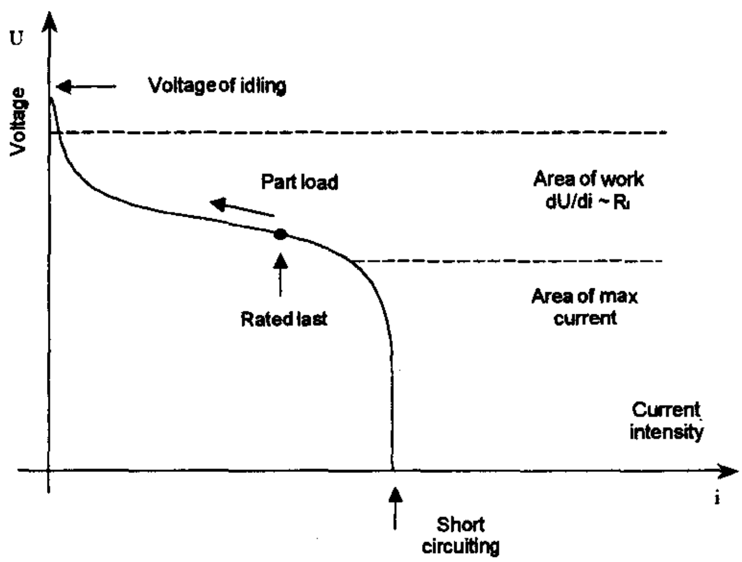

Fig.5. Current – voltage characteristics of single $H_2 - O_2$ fuel – cell

3. Application of fuel-cell to automotive vehicles

3.1. Fuel-cell: present status

Application of fuel-cell (FC) to automotive vehicles is considered as prime mover, but also as the power in hybrid-electric vehicles and as auxilliary power for electronic and electric devices on board vehicle. Application of FC to vehicles is determined by development of their technology, their weight, size and electric parameters, which should by improved. Also the containers of fuel, especially hydrogen, of which density of energy storage as well as the rate of fuel energy for start should by higher. Energy density of contemporary FC is of the order 10 kW/kg and 1,0 kW/dm^3 [3]. Efficiency of FC is shown in Fig.6; if is much more better than conventional IC engines, especially for part load.

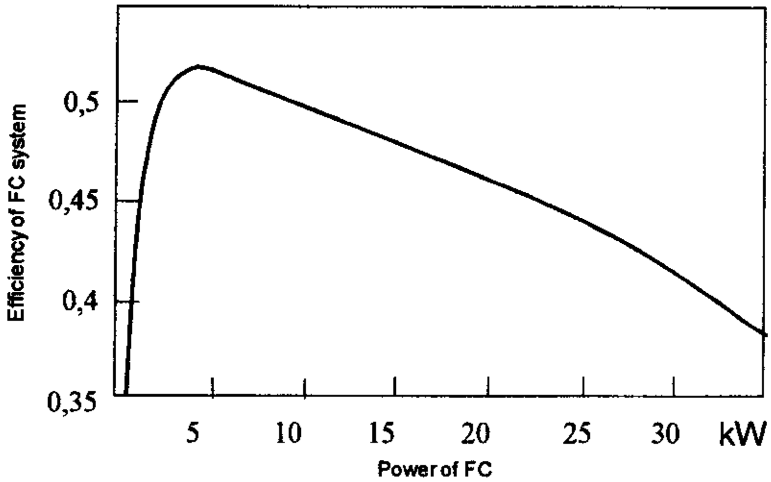

Fig. 6. Efficiency versus total power of a fuel cell system, modelled a 35 kW_{el} system [4]

FC are being developed by specialised companies, like Ballard, which established precompetitive development venture – XCELLSiS (which spent 1 bilion USD for R&D work) and American – Global Alternative Propulsion Center (GAPC), which employs 200 engineers in USA and Germany. Companies: Toyota, Honda, Nissan and Mitsubishi have their own Japan center to devolop FC. Ballard develops hydrogen PEM FC. During working on FC, Ballard obtained 400 patents in PEM FC technology. Power density of new Mark 900 FC is as much as 1,35 kW/dm^3 (former Mark 700 FC - 1,0 kW/dm^3).

GAPC develops methanol FC for GM and Daimler Chrysler. Presently more than 20 companies develop FC.

As for as auxiliary energy source are concerned, BMW first installed FC in 750i car to meet the needs of electronic systems. Gasoline SOFC operates at 800 °C via circonium oxide ceramics. FC uses 0.7 dm^3 per 100 km (normally SI engine used 1,5 dm^3 gasoline to power electric systems).

3.2. Hydrogen fuel-cell as prime mover

Daimler-Chrysler [3]. The simplest fuel-cell is that, which usues hydrogen. Both, the hydrogen gas and atmosferic air can be supplied directly to fuel stack without prior treatment. Such fuel-cells are developed by the most of companies, including Daimler-Chrysler [3] – Table 3. For the electrolyte solid polimer (SPFC) or proton membrane (PEM FC) are used. FC is installed in Mercedes-Benz Klasse A car.

Table 3. Overview of fuel cell demonstration cars developed by Daimler Chrysler, based on different onborad fuel storage concepts [4]

	Year	Fuel	Number of stacks	Voltage	Power of the system	Power/ /Mass
NECAR I	1984	Hydrogen	12	230 V	50 kW	21 kg/kW
NECAR II	1986	Hydrogen	2	280 V	50 kW	6 kg/kW
NEBUS	1987	Hydrogen	10	720 V	250 kW	5,6 kg/kW
NECAR 3	1987	Methanol	2	300 V	50 kW	15 kg/kW
JEEP COM-MANDER STUDY	1988	Gasoline	1	250 V	50 kW	39 kg/kW
NECAR 4	1999	Liquid hydrogen	2	330 V	70 kW	5 kg/kW
NECAR 4	2000	Methanol	1	250 V	75 kW	-

Renault [5]. Renault design od fuel-cell is based on hydrogen stored in liquid state in cryogenic containers in temperature of –253°C. Start-up and top power are provided by nickel/metal-hydrid batteries. The fuel-cell has an output of 30 kW at 90 V, an inverter changes the output from DC to AC and a transformer increases output voltage to 250 V to supply to a synchronous electric motor driving through a fixed ratio transmission. In future, Renault fuel-cell car will be fuelled with liquid hydrocarbon fuels and methanol.

VW [3]. Volkswagen introduced fuel-cell to Bora car. Capacity of fuel tank is 49 dm^3 of hydrogen.

Honda, Nissan, Ford [3]. Hydrogen FC is being installed also in Honda FCX-V3, Nissan Xterra FC and Ford Focus research vechicles.

3.3. Methanol fuel-cell

General Motors [3, 6]. GAPC of General Motors Europe is now running a fuel-cell-powered technology on new Opel car Zafira. The fuel-cell is fuelled now with methanol, but other fuels are being concidered, including synthetic gasoline. In a very long term, hydrogen produced with the aid of solar energy as an input is conceivable. In the above system, methanol is reformed and hyrogen and carbon dioxide are produced:

$$CH_3OH \rightarrow 2H_2 + CO$$

The oxygen is supplied in an atmospheric air by the use of compressor. Hydrogen and oxygen reacts at temperature 80-90°C to form water. Single cells are combined in a stack and there is sufficient energy to power 50 kW synchronous electric motor. The amount of carbon dioxide is 50% less than that of CI engine.

GAPC scientists are now being focussed on the problem of cold start (say to –30°C) and conditions of extreme humidity. A battery is fited to meet higher power demands and speeds start-up. For Zafira start up time is 20 s, what is unacceptable, it should be a couple of seconds. Production fuel-cell car would not have battery.

Zafira has a top speed 120 km/h with 50 kW. The range of production fuel-cell vehicle would be 1000 km, as for Opel regular IC engine car. GM's GAPC's fuel-cell system based on methanol is shown in Fig.7.

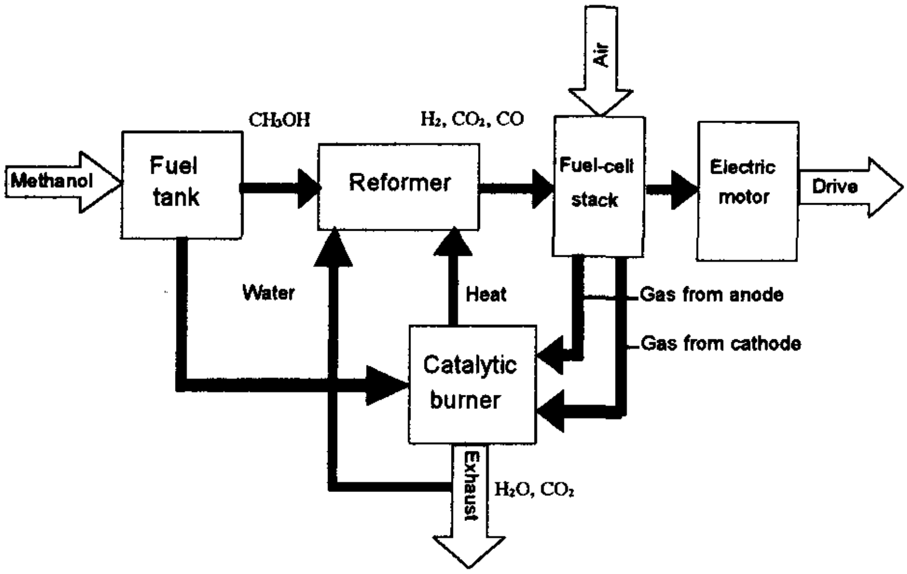

Fig. 7. GME's example of function principle of methanol powered fuel cell system

The fuel-cell system is placed in the rear and under the hood and floor.

Daimler-Chrysler [3]. Also Daimler-Chrysler develops vehicle powered by methanol fuel-cell – Jeep Commander 2 SUV. It has two Ballard Mark 700 fuel-cell stack. It is hybrid-electric vehicle, because it is supplied in 90 kW nickel/metal hydride battery pack to provide a power assist boost for acceleration and towing.

Honda [3]. Also Honda applied methanol fuel-cell to research vehicle FCX-V2.

3.4. Gasoline fuel-cell

On of the first gasoline fuel-cell is that of Chrysler Corporation [6]. Hydrogen is processed from gasoline onboard vehicles, because it isn't "practical fuel choice today" and takes up a lot of space.

The Chrysler fuel-processing technology essentially converts gasoline into hydrogen H_2, carbon dioxide CO_2 and water H_2O in a multistage chemical process. Other fuels can be used: diesel fuel, methane and alcohols, because "processor can burn anything". Power comes from a stack of fuel cells energising electric motor driving the rear wheels. The fuel-cell stack is modular and can be configured into a wide array of shapes. Fuel processing is as follows. Fuel is heated to convert it to gas in a fuel burner/vaporiser (canister ϕ150x500 mm). The vaporised gasoline is processed in a partial oxidation (POX). The reactor is canister (ϕ350x560 mm), in which gasoline vapour is ignited by spark plug to initiate a partial burning in a low pressure environment. By limiting the amount of air, hydrogen and carbon monoxide are produced. Sulphur in the gasoline is converted into hydrogen sulphide gas and then filtered from the vapour. Since CO poisons fuel-cell it must be eliminated or reduced to extremely low level (< 10 ppm). It is done by the use of water as a steam acting with the catalyst: copper oxide and zinc oxide, to oxidise CO to CO_2. Additionally hydrogen is produced also in this stage. Then the vapour is treated by injected air, which reacts with remaining CO over platinum catalyst to produce CO_2. The process requires a heat exchanger to maintain temperature of 80°C – at which fuel-cell has the best efficiency. The by-products of the processing are: CO_2, N_2 and H_2O. The layout of Chrysler automotive fuel-cell is shown in Fig.8.

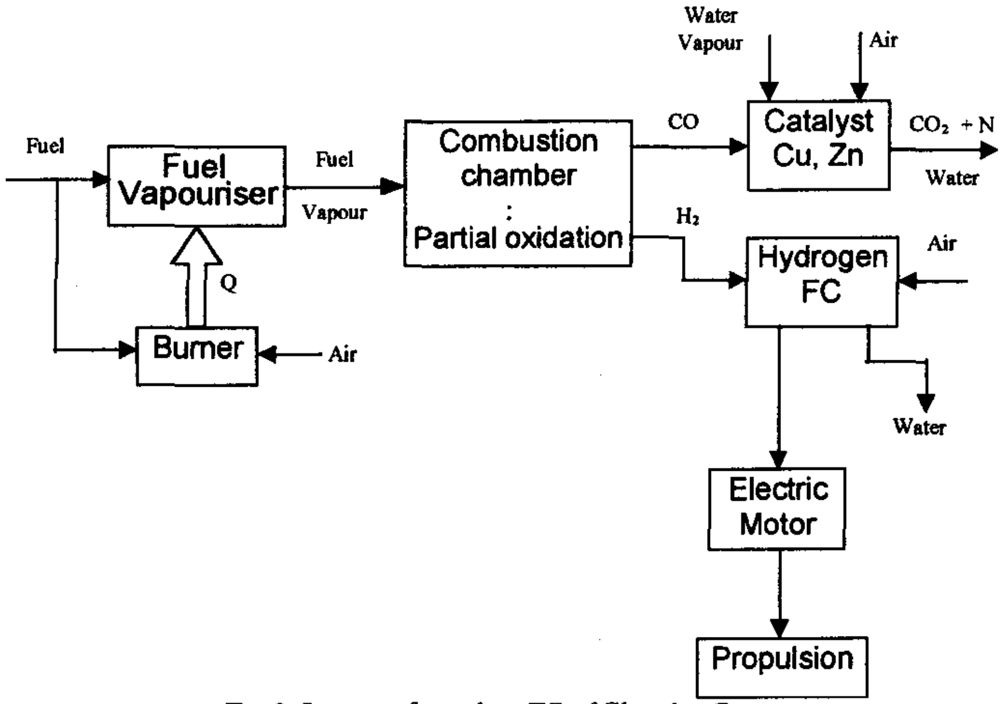

Fig.8. Layout of gasoline FC of Chrysler Corp.

4. Development forcast of fuel-cell

Fuel-cell vehicle is the only alternative for zero emission vehicle (ZEV). Development of fuel-cell vehicle (FCV) is out of discussion, but the problem is in the fuel to FC and how to store it onboard vehicle. Also very serious problem is to build infrastructure – filling stations. Fuel option for fuel-cell is shown in Fig.9.

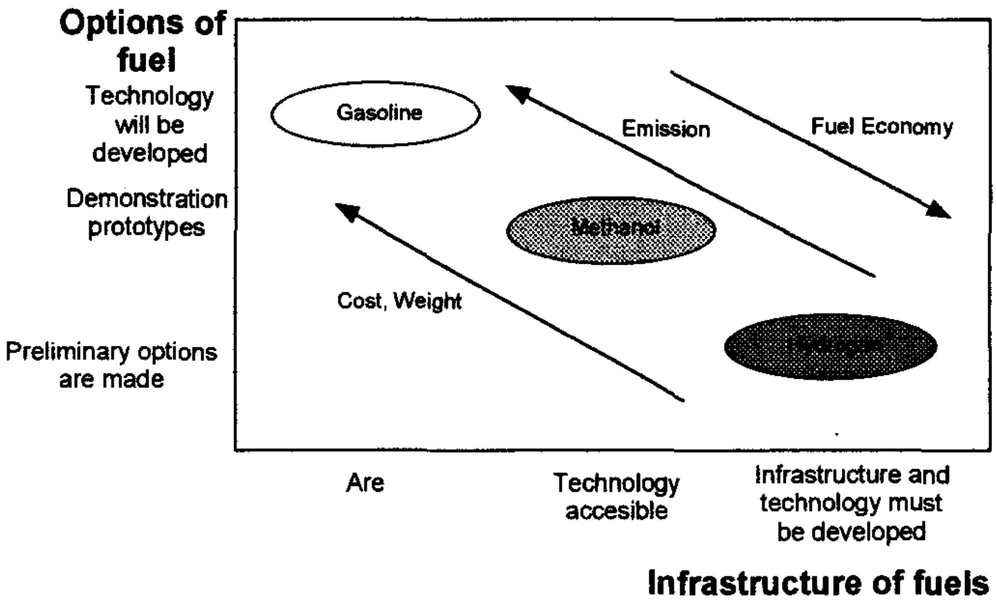

Fig.9. Fuel option for FC in automotive applications versus infrastructure cost [4]

First gasoline FC will be introduced to production vehicles, due to its multiplicity in the market. Next will be methanol and then hydrogen, the fuel of future.

First FCV will appear in the year 2004. Scenario of market FC cars is shown in Fig.10. FCV will be introduced to the market step by step.

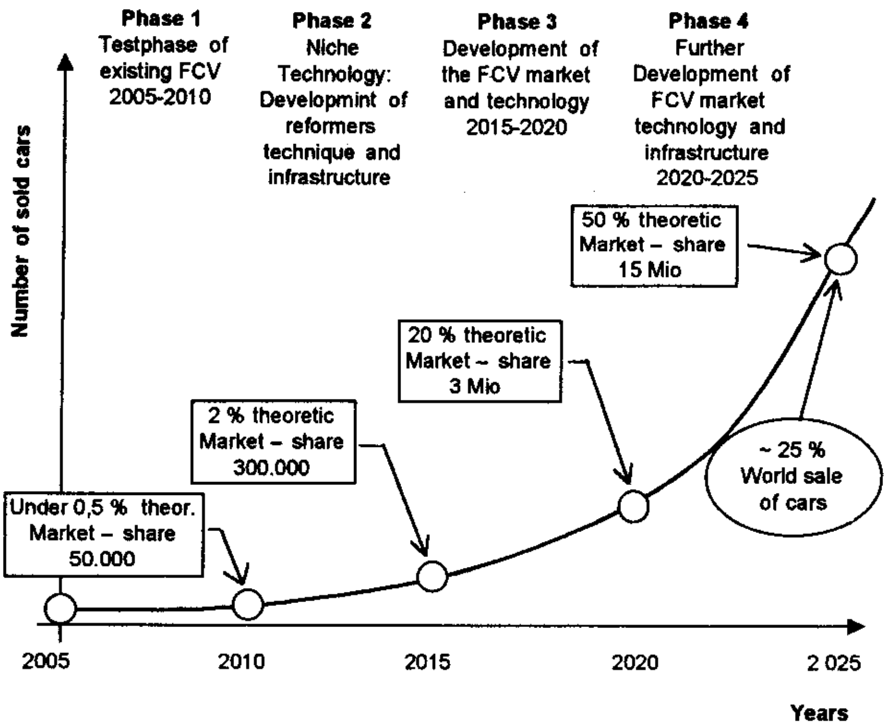

Fig.10. Market scenario of fuel cell cars [7]

5. Conclusion

- Fuel-cell convert potential chemical energy of the fuel into electrical energy without need for transfer it into heat in low temperature process.
- Theoretical efficiency of fuel-cell is very high and not limited by efficiency of Carnot cycle.
- Due to low temperature of electrochemical reactions and hydrogen as a fuel, FC is practically zero emission power source (emission of CO is very low).
- Emission of greenhouse gas (CO_2) for hydrogen fuel-cell is much more lower for methanol or gasoline fuel-cell then for conventional IC engine.
- At present the most advanced are research vehicles powered with hydrogen FC.
- First into the market gasoline FCV will be introduced due to existing fuel market.

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