FUEL CELLS TECHNOLOGY SCAN

Fuel cells are the most efficient and extremely clean systems for generation from fossil fuels. Fuel cell is an electrochemical device that converts chemical energy of a fuel directly into electrical energy. It has two electrodes where electrochemical reactions occur in a reservoir of electrolyte that allow ions to flow between the two electrodes producing DC electricity. Fuel cells were initially used for power generation in spacecrafts.

The major advantages of fuel cells are :

- The commercial fuel cell power plants offer the highest net efficiencies in the range of 50-70% on upto 11MW capacity. The waste heat generated in the form of steam produced during exothermic electrode reactions, can further be utilised to enhance the overall efficiency to >70%. The efficiency of fuel cells remains constant irrespective of the size and power plants can be configured for a wide range of outputs ranging from few watts to several megawatts.

- Since the combustion of fuel gas does not occur in a fuel cell the emission of NOx/SOx is negligible. Moreover the fuel gas can be cleaned before being fed to the fuel cell minimising the particulate & SOx emission.

- Fuel cells have least moving parts (only compressor), resulting in noise free operation and little maintenance.

- Fuel cells have high output to weight & volume ratios which are helpful in their application to transport sectors and installation in densely populated areas.

- Fuel cells have quick load following capabilities and comparatively higher part load efficiencies.

Constituents of a Fuel Cell Power Plant:

1. Reformer section to process hydrocarbon fuel for fuel cell use.

2. Power section to convert chemical energy of processed fuel into DC power.

The output of a fuel cell is DC electricity of very low voltage of less than one volt. Practical voltages are obtained by connecting a number of fuel cells in series.

3. Inverter to convert DC to AC power supply.

4. Support operations like condensation of process water, waste heat removal, steam generation etc.

Fuel Cell Types :

Fuel Cells can be classified according to the type of ionic conductor they use (e.g. PAFC, MCFC, SOFC etc.) and the temperature range (i.e., high, medium & low temperature) at which they operate.

Phosphoric acid concentrated to 100% is used for the electrolyte in this fuel cell, which operates at 150 to 220 ^{0}C. At lower temperatures, phosphoric acid is a poor ionic conductor, and CO poisoning of the Pt electrocatalyst in the anode becomes severe. The relative stability of concentrated phosphoric acid is high compared to other common acids; consequently the PAFC is capable of operating at the high end of the acid temperature range (100 to 220 ^{0}C). Phosphoric Acid Fuel Cells (PAFCs) are the most mature fuel cell technology. Through organizational linkages with Gas Research Institute (GRI), electric utilities, energy service companies, and user groups, DOE has helped in bringing about commercialization of the world's first fuel cell produced by ONSI. Turnkey 200-kilowatt plants are now available and have been installed at more than 100 sites in the United States, Europe, and Japan. Operating at about 200^{0}C (400^{0}F), the PAFC plant also produces heat for domestic hot water and space heating, and its electrical efficiency is 36-38 percent.

A molten carbonate fuel cell (MCFC) uses a carbonate electrolyte (generally of lithium and potassium carbonates) and operates at approximately 650^{0}C (1200^{0}F). The high operating temperature is needed to achieve sufficient conductivity of the electrolyte. Because of this high temperature, noble metal catalysts are not required for the cell electrochemical oxidation and reduction processes. Molten carbonate fuel cells are being developed for natural gas and coal based power plants for the industrial and electric utility sectors. The MCFC is often referred to as a second generation fuel cell because it is expected to reach commercialization after Phosphoric Acid Fuel Cells (PAFCs) are available in the marketplace. Currently, three industrial corporations are actively pursuing the commercialization of MCFCs in the United States; these are Energy Research Corporation, International Fuel Cells Corporation, and M-C Power Corporation. Molten Carbonate Fuel Cells (MCFCs) are now being tested in full-scale demonstration plants. They offer higher fuel-to-electricity efficiencies, approaching 60%. MCFCs operate at higher temperatures, around 650^{0}C (1,200^{0}F), making them candidates for combined-cycle applications, in which the exhaust heat is used to generate additional electricity. When the waste heat is used for co-generation, total thermal efficiencies can approach 85%.

The solid oxide fuel cell using a ceramic electrolyte of yttria stabilized zirconia operates at about 1000^{0}C (1800^{0}F). The attractiveness of this cell relates principally to its solid state nature, its potential to reform gaseous fuel within the cells and its high operating temperature which can provide high quality heat for energy conversion or other uses. The solid electrolyte eliminates problems of electrolyte containment, electrolyte migration, and allows designs which utilize the electrolyte as part of the structural members of the cells. Solid oxide fuel cells (SOFCs) have emerged as a serious alternative high temperature technology contender. Of primary importance, is that the electrolyte is in a solid phase and not a liquid electrolyte with its attendant material corrosion and electrolyte management problems. The operating temperature of 1000C allows internal reforming, promotes rapid kinetics with nonprecious materials, and produces high quality byproduct heat for cogeneration or for use in a bottoming cycle, similar to the Molten Carbonate Fuel Cell (MCFC). However, the high temperature of the SOFC places stringent requirements on its materials. The development of suitable materials and the fabrication of ceramic structures are presently the key technical challenges facing SOFCs.

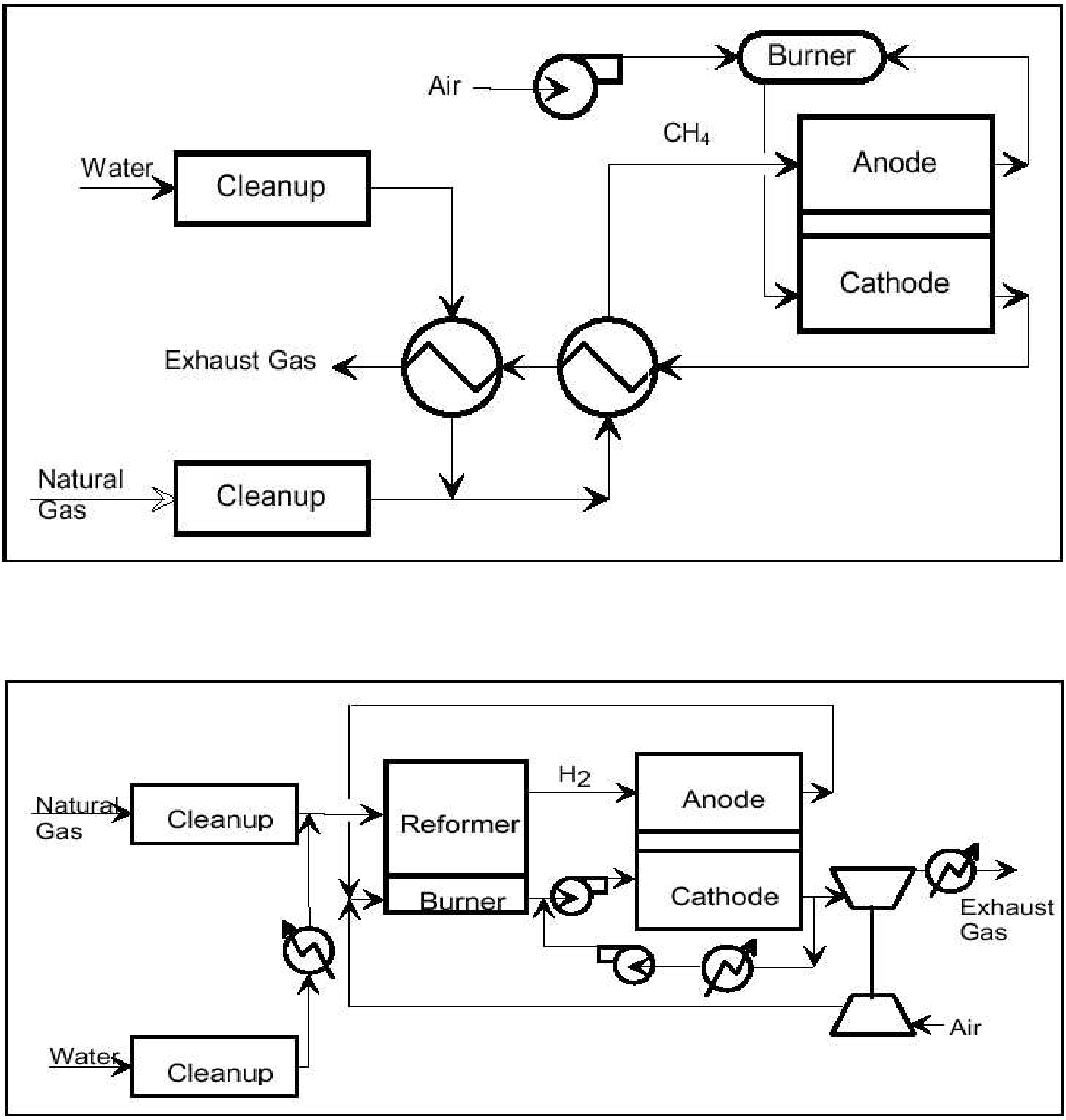
Solid Oxide Fuel Cells (SOFCs) are currently being demonstrated in a 100-kilowatt plant. This fuel cell technology offers stability and reliability of all-solid-state ceramic construction. High-temperature operation, up to 1,000^{0}C (1,800^{0}F), allows more flexibility in the choice of fuels and can produce very good performance in combined-cycle applications. Adjusting air and fuel flows allows the SOFC to easily follow changing load requirements. Like MCFCs, SOFCs approach 60% electrical efficiency in the simple cycle system, and 85% total thermal efficiency in co-generation applications.

	Phosphoric Acid	**Molten Carbonate**	**Solid Oxide**
Electrolyte	Phosphoric acid	62% $LiCO_3$ & 38%K_2 CO_3	Yttrium - stabilised Zirconia
Anode	Pt/C/	Ni-10% Cr	Ni-ZrO_2 cermet
Cathode	Pt/C	Li-doped NiO	Sr-doped LaMn O_3
Pressure	1-10 bar	1-10 bar	1 bar
Operating Temperature	260^0C	650^0C	1000^0C
Material of Cell	Carbon	Ni, stainless steel	Ceramics
Fuel to Electrical Efficiency Simple Cycle (LHV) Combined Cycle (LHV)	 40% 44%	 55% 50-65%	 50% 45-65%
Reactant Fuels	H_2	H_2 , CO	H_2 , CO, natural gas
Applications	Power generation, transport	Power generation (base load)	Power generation
Technology Status	Nearly commercial	Development stage	Development stage

Note: A detailed comparison of all types of fuel cells is enclosed at Annexure

Reformation in Fuel Cells:

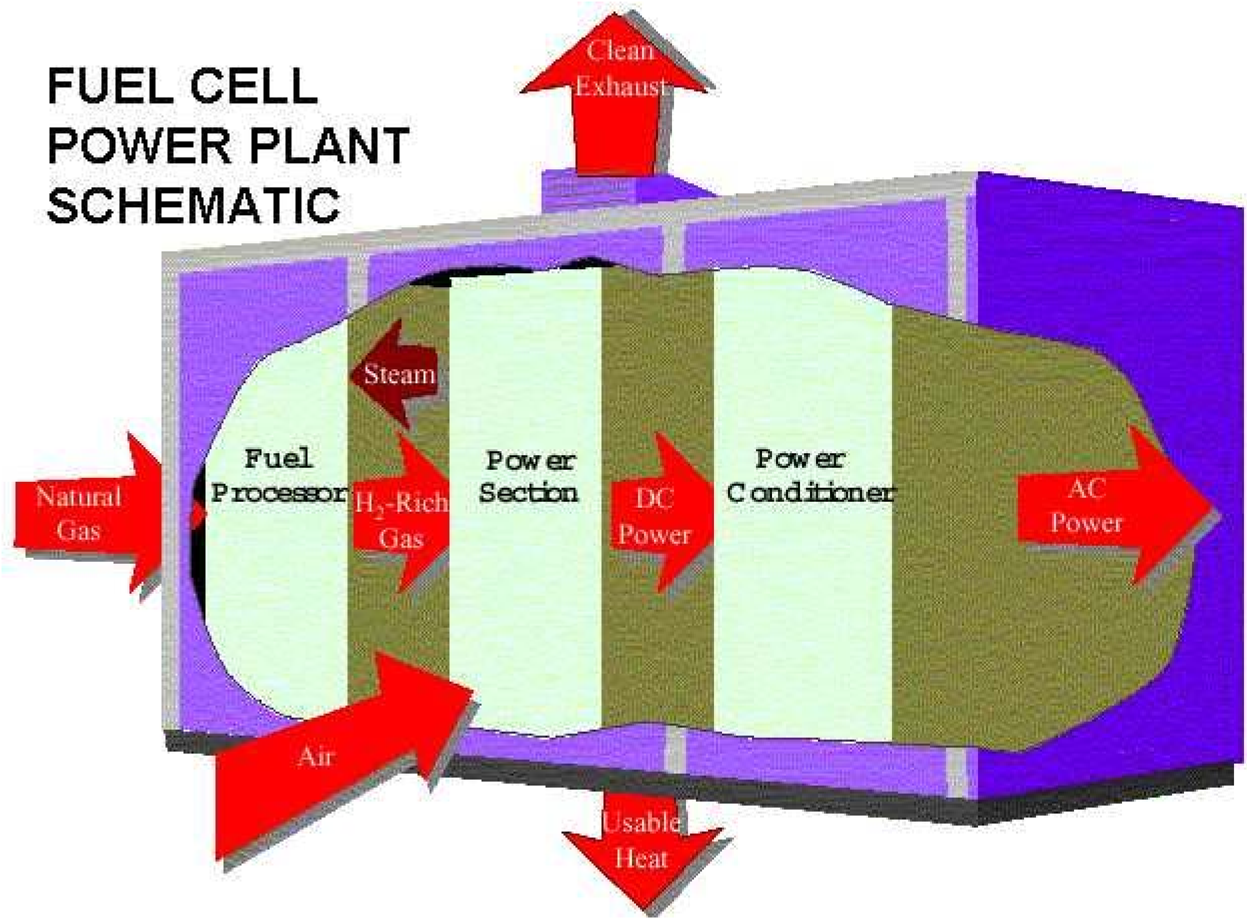
Even though the electrolyte has become the predominant means of characterizing a cell, another important distinction is the method used to produce hydrogen for the cell reaction. Hydrogen can be reformed from natural gas and steam in the presence of a catalyst starting at a temperature of ~760^0C. The reaction is endothermic. MCFC, ITSOFC (Intermediate Temperature Solid Oxide Fuel Cell), and TSOFC (Tubular Solid Oxide Fuel Cell) operating temperatures are high enough that reforming reactions can occur within the cell, a process referred to as internal reforming. Figures below show a comparison of internal reforming and external reforming MCFCs. The reforming reaction is driven by the decrease in hydrogen as the cell produces power. This internal reforming can be beneficial to system efficiency because there is an effective transfer of heat from the exothermic cell reaction to satisfy the endothermic reforming reaction. A reforming catalyst is needed adjacent to the anode gas chamber for the reaction to occur. The cost of an external reformer is eliminated and system efficiency is improved, but at the expense of a more complex cell configuration and increased maintenance issues. This provides developers of high-temperature cells a choice of an external reforming or internal reforming approach. The present internal reforming MCFC is limited to ambient pressure operation, whereas external reforming MCFC can operate at pressures up to 3 atmospheres. The slow rate of the reforming reaction makes internal reforming impractical in the lower temperature cells. Instead, a separate external reformer is used.



Schematics of External & internal Reforming

DESCRIPTION OF A FUEL CELL BASED POWER PLANT

The fuel cell combines hydrogen produced from the fuel and oxygen from the air to produce dc power, water, and heat. In cases where CO and CH_4 are reacted in the cell to produce hydrogen, CO_2 is also a product. These reactions must be carried out at a suitable temperature and pressure for fuel cell operation. A system must be built around the fuel cells to supply air and clean fuel, convert the power to a more usable form such as grid quality ac power, and remove the depleted reactants and heat that are produced by the reactions in the cells. Figure below shows a simple representation of a fuel cell power plant. Beginning with fuel processing, a conventional fuel (natural gas, other gaseous hydrocarbons, methanol, naphtha, or coal) is cleaned, then converted into a gas containing hydrogen. Energy conversion occurs when DC electricity is generated by means of individual fuel cells combined in stacks or bundles. A varying number of cells or stacks can be matched to a particular power application. Finally, power conditioning converts the electric power from dc into regulated dc or ac for consumer use.



A wide spectrum of contaminants is present in coal-derived fuel gas. The removal of these contaminants can add considerably to the efficiency.

CONTAMINANTS FROM COAL-DERIVED FUEL GAS AND THEIR POTENTIAL EFFECT ON MCFC FUEL CELL

Class	**Contaminant**	**Potential Effect**
Particulates	Coal fines, ash	Plugging of gas passages
Sulfur compounds	H_2S, COS, CS_2, C_4H_4S	Voltage losses Reaction with electrolyte via SO_2
Halides	HCl, HF, HBr, $SnCl_2$	Corrosion Reaction with electrolyte
Nitrogen compounds	NH_3, HCN, N_2	Reaction with electrolyte via NOx

Trace metals	As, Pb, Hg, Cd, Sn Zn, H_2Se, H_2Te, AsH_3	Deposits on electrode Reaction with electrolyte
Hydrocarbons	C_6H_6, $C_{10}H_8$, $C_{14}H_{10}$	Carbon deposition

Status of Fuel Cell Technology :

While phosphoric acid fuel cell (PAFC) is nearest to commercialisation and has been demonstrated in 40kW to 11 MW sizes. Molten Carbonate Fuel Cell (MCFC) and Solid Oxide Fuel Cell (SOFC) are in development stage and have been demonstrated on 250kW scale.

In Japan, over 100 PAFC plants ranging from 50kW to 500kW capacity have been developed & installed over the last six years. The largest demonstration PAFC plant is also in Japan of 11MW capacity run by Tokyo Electric Company. In Europe, there are ten International Fuel Cells Inc. (IFC) PC25 200kW power units currently undergoing demonstration. Fuji Electric Company and Mitsubishi Electric Company are the leading manufacturers in Japan.

In the US MC-Power Corporation was set up to commercialise the MCFC technology developed by the Institute of Gas Technology (IGT) in Chicago. MC-Power is currently commissioning two major demonstration plants at 250kW scale, one by Unocal and other by San Diego Gas & Electric Co. Energy Research Corporation, USA has provided the technology for another demonstration at 1MW scale at Santa Clara, California. Dutch Fuel Cell Corporation in an EC-Joule III programme is leading the advanced MCFC program which began in 1996. Partners in this development are British Gas, Gaz de France & Sydkraft. In Germany, a consortium led by MBB-Deutsche Aerospace is developing ERC technology for the European market. Leading developers in Japan are Mitsubishi Electric, Hitachi. Other manufacturers include IHI, Toshiba, Ebara Corp and Kawasaki Heavy Industries.

In one of the latest developments, in June 2000, a 220kW demonstration Integrated Gasification SOFC plant has been commissioned at US National Fuel Cell Research Center, Irvine, California. It consists of a Siemens-Westinghouse fuel cell integrated with a GE microturbine. Once commercialised the gasification-fuel cell hybrid systems are expected to cost around $ 1300 -1500/kW.

LIST OF SOME MAJOR FUEL CELL BASED PLANTS:

S. No.	Power Plant	Capacity	Fuel Cell Type	Year of Operation	Remarks
1.	Westervoort, Netherlands	100 kW	SOFC	December, 1997	Westinghouse Commercial scale Demonstration Plant
2.	Japan	11 MW	PAFC		Largest Demonstration plant
3.	Chugach Electric Association, Alaska, USA	1MW	PAFC (5 X 200kW)	August 1999	IFC PC25 fuel cells
4.	Santa Clara, California, Energy	2 MW	MCFC	April, 1996	ERC demonstration plant. (achieved 44%

	Research Corporation(ERC)				efficiency)
5.	US National Fuel Cell Research Centre, Irvine, California	220kW	Integrated Gasification SOFC	June, 2000	Prototype, Siemens Westinghouse fuel cell, GE microturbine

Emission Levels :

The following table compares emissions of Fuel Cells with other conventional fossil fuel power generation technologies.

Pollutants gm/MWh	**Pulverised coal**	**Oil fired**	**Gas fired**	**IGCC**	**Fuel cell**
Air Particulate	410	420	450	6	6
NOx	2890	1250	890	185	20
SOx	4950	3350	----	30	26

Economic Aspects :

The capital cost of PAFC is projected to be $3000/kW, while that of MOFC $1300/kW. The manufacture of hydrogen from fossil fuels is accompanied by carbon monoxide & dioxide. PAFC requires pure hydrogen while MCFC & SOFC can handle mixtures of CO & H_2. The life span of a fuel cell stack is roughly 5 years while that of balance of plant is about 30 years. Therefore six sets of fuel cell sets are required during the plant life span. This increases the capital cost of fuel cell power plants considerably. Improvements in fuel cell stack life is essential for better economics.

LOW TEMPERATURE FUEL CELLS

	AFC (Alkaline)	PEMFC (Proton Exchange Membrane)	DMFC (Direct Methanol)
Charge carrier	OH^- (aq)	H^+ (aq)	H^+ (aq)
Electrolyte	Concentrated KOH solution (35-40 wt%)	Perfluorinated solid polymer membrane	Perfluorinated solid polymer membrane
Temperature(°C)	70-90	70-90	70-90
Anode reaction	$H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-$	$H_2(g) \rightarrow 2H^+(aq) + 2e^-$	$CH_3OH(aq) + H_2O(l) \rightarrow CO_a(g) + 6H^+(aq) + 6e^-$
Cathode reaction	$½O_2(g) + 2H_2O(l) + 2e^- \rightarrow 2OH^-(aq)$	$½O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O(l)$	$6H^+(aq) + 6e^- + {}^3/_2O_2(g) \rightarrow 3H_2O(l)$
Overall reaction	$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$	$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$	$CH_3OH(aq) + {}^3/_2O_2(g) \rightarrow CO_a(g) + 2H_2O(l)$
Δ G (kJ mol^{-1})	-237.3	-237.3	-702.5
Δ H (kJ mol^{-1})	-286.0	-286.0	-726.6
E_{rev} (V)	1.229	1.229	1.214
η_{ideal} %	83.0	83.0	96.7
Sys. Efficiency (%)	55-60	32-40	35-40
Power levels (kW)	50-100	0.1 - 250	<1 (Lab prototypes)
Price (US$/kW)	2,000-3,000	500-1000	?
Applications	Space (NASA), terrestrial transport (UK cabs, and German submarines)	Mobile (buses and cars), portable power, military, domestic (homes, hotels, hospitals), medium to large scale stationary.	Same as PEMFCs
R&D and Commercial Developers	Pratt & Whitney, Union Carbide (US), GEC (France), Siemens (Germany), Elenco (now Zevco — Belgium), K. Kordesch (Austria), Fuji (Japan).	Ballard, U. of Victoria (Canada), International FCs, Plug Power, GM, Energy Partners, Allied Signal, H Power (US), Siemens (Germany), De Nora (Italy), ECN (The Netherlands), Loughborough U. (UK), Sanyo, Toyota, Honda (Japan)	Jet Propulsion Laboratory, Los Alamos Natl. Lab. (US), Siemens (Germany),
Status	Mature technology struggling to	Pre-commercial, receiving the	Laboratory prototypes

	penetrate markets and facing strong competition form PEMFCs.	most attention for mobile and portable applications. Stationary applications to benefit from progress in other areas.	
Advantages	Inexpensive materials, CO tolerance, faster cathode kinetics	High power densities, proven long operating life, adopted by major automakers	Reduced overall system complexity (fuel reforming, compression, and humidification are eliminated)
Disadvantages	Corrosive liquid electrolyte, CO_2 intolerant	CO intolerance, Water/heat management, Expensive catalyst	Complex stack structure, noble catalyst required

MEDIUM AND HIGH TEMPERATURE FUEL CELLS

	PAFC (Phosphoric Acid)	MCFC (Molten Carbonate)	SOFC (Solid Oxide)
Charge carrier	$H^+(aq)$	CO_3^{2-} retained in a ceramic matrix (e.g., $LiAlO_2$)	Mobile O^{2-} ions migrating through crystal lattice
Electrolyte	Concentrated H_3PO_4 solution (95-98%)	Molten salt (e.g., Li_2CO_3/Na_2CO_3)	Yttria-stabilised ZrO_2
Temperature (° C)	150-210	550-650 (practical), 800-900 (optimal)	800-1,100
Anode reaction	$H_2(g) \rightarrow 2H^+(aq) + 2e^-$	$H_2(g) + CO_3^{2-} \rightarrow CO_2\,(g) + H_2O(g) + 2e^-$	$H_2(g) + O^{2-} \rightarrow H_2O(g) + 2e^-$
Cathode reaction	$½O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O(l)$	$2e^- + CO_2\,(g) + ½O_2\,(g) \rightarrow CO_3^{2-}$	$½O_2\,(g) + 2e^- \rightarrow O^{2-}$
Overall reaction	$H_2(g) + ½O_2(g) \rightarrow H_2O(l)$	$H_2(g) + CO_2(g) + ½O_2\,(g) \rightarrow CO_2\,(g) + H_2O(g)$	$H_2(g) + ½O_2(g) \rightarrow H_2O(g)$
Δ G (kJ mol^{-1})	-237.3		-237.3
Δ H (kJ mol^{-1})	-286.0		-286.0
E_{rev} (V)	1.229		1.229
η_{ideal} %	83.0		83.0
Sys. Efficiency(%)	36-45	50-60	50-55 (70-80 in combined cycles)
Power levels (kW)	$10 - 10^7$	$10^2 - 10^5$	$10^2 - 10^5$
Price (US$/kW)		?	?
Applications	Medium and large scale co-generation plants	Large scale power generation, co-generation	Medium to large scale power generation, CHP, combined turbine cycles

R&D and Commercial Developers	Japan: Fuji, Toshiba, Hitachi, Mitsubishi Electric, Tepko, Osaka Gas. US: UTC (ONSI and IFCs)	Energy Research Corporation, M-C Power Corporation, Intl. Fuel Cells (USA), IHI, Mitsubishi Electric, Sanyo (Japan), MTU (Europe), Ansaldo (Italy), ECN (The Netherlands) BG Technology (UK)	Global Thermoelectric (Canada), Sulzer (Switzerland), Siemens-Westinhouse (tubular, USA/Germany), Ztek, Sofco (US), Mitsubishi (Japan), Ceramic Fuel Cells (Australia), BG Technology (planar, UK)
Status	First generation technology. Commercially available. Will face strong competition from other FC technologies	Well developed. Semi commercial	Least developed of all technologies (excepting, perhaps, DMFCs).
Advantages	Commercially available, market presence, proven life.	High efficiency, internal fuel processing, high grade waste heat	High efficiency, internal fuel processing, high grade waste heat
Disadvantages	Relatively low efficiency Limited lifetime Expensive catalyst	Electrolyte instability Lifetime undetermined	High operating temperature (materials), High cost, Low specific power

Reference :

1) Proceedings of Ist International Conference Green Power- The Need for the 21st Century 12-14 February, 1997 New Delhi
2) Fuel Cell Handbook (Fifth Edition) By EG&G Services Parsons, Inc. for NETL, USDOE.
3) Joint Fuel Cell Technology Review Conference 1999 - Technical Papers. (http://www.fetc.doe.gov)