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Fuel Cell Technology Overview Study and Evaluation.

Helmy El-Sayed Gad

Mechanical Power Engineering., Faculty of Engineering., El-Mansoura University., Mansoura., Egypt

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FUEL CELL TECHNOLOGY
OVERVIEW STUDY AND EVALUATION

دراسة وتقيم تكنولوجيا خلايا الوقود

H. E. Gad
Mechanical Power Engineering Department,
Faculty of Engineering, Mansoura University.

ملخص البحث

لقد وصل تلوث الهواء فى التجمعات السكانية الكبيرة على مدى العقود القليلة الأخيرة إلى مستويات حرجة للغاية. وسائل النقل، توليد الطاقة والأنشطة المدنية والصناعية الأخرى هى المسئولة عن هذا المستوى المأساوى للتلوث. وكان ظهور خلايا الوقود وسيلة جديدة لإشباع الرغبة المتزايدة فى توليد الطاقة والمحافظة فى نفس الوقت على بيئة نظيفة. يرجع ذلك إلى أن خلية الوقود هى وحدة تحويل مباشر من الطاقة الكيميائية للوقود إلى طاقة كهربية، دون التحويل أولاً إلى حرارة. يتناول هذا البحث تطبيق تقنية خلايا الوقود، نظرية العمل، التصنيف واختبار مناسبتها لتوليد الطاقة لكل من الوحدات الثابتة والمتنقلة والمحمولة. وقد تم عمل مقارنات بين أنظمة خلايا الوقود المختلفة بطريقة تتيح سهولة البحث وسرعة الاختيار. وقد تمت أيضاً مناقشة الحدود والعقبات التقنية التى يجب التغلب عليها لانتشار وتطبيق خلايا الوقود فى النقل وتوليد الطاقة. كما تمت مناقشة تطبيق قوانين الديناميكا الحرارية فى تحليل وأداء خلايا الوقود. وقد خلصت هذه الدراسة إلى أن تقنيات خلايا الوقود هى واعدة للغاية، كما أنها وبفضل مزيد من الأبحاث سوف تستطيع التغلب على كل عقبات التطبيق الاقتصادى والتجارى، وتحدث ثورة علمية وتكنولوجية كالتى أحدثها الميكروبروسيسور.

ABSTRACT

The air pollution in large communities has reached a critical state in the last few decades. Transportation, power generation and other civil and industrial activities are responsible of this drastic pollution. The fuel cell technology has come as a new approach to satisfy the ever increasing thirst for power generation and, in the same time, keeping a clean environment. The fuel cell is a direct energy conversion unit from the fuel chemical energy to electrical energy, without conversion first to heat. This paper deal with fuel cell technology, theory of operation, classification and examine its suitability for stationary, mobile and portable power generation units. Comparison between different fuel cell systems is carried out in a systematic way to enable quick search and selection. The paper discusses also the technical limitations to be overcome for the wide application of the fuel cell in transportation and power generation. Application of thermodynamics laws on the fuel cell to analyze its performance has been discussed. The paper concludes that the future of this technology is extremely promising. Therefore, very serious efforts in fuel cell researches are needed to overcome difficulties for commercialization. The fuel cell should be considered as a revolution transforming our science and technology just as that of microprocessor.

INTRODUCTION

Without a combustion process, the fuel cell is a device that produces electrical power (direct current) when it is supplied with fuel and Oxygen. Electrochemical reactions at its ele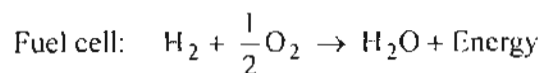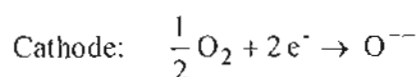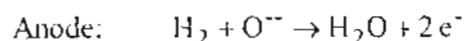ctrodes produce also heat and potable water as a byproduct. The Fuel cells have obvious advantages in high efficiency and clean operation. A typical fuel cell consists of a negative electrode (anode), a positive electrode (cathode), and the electrolyte in between as shown in Fig. 1. The anode provides an interface between the fuel and

system complexity and improve the thermal management of PEMFC systems.

5- Solid Oxide fuel cells (SOFC)

Solid oxide fuel cell is a high temperature fuel cell (operating temperature ranges from 900 to 1000 C). Therefore, it is suitable for power generation, with an efficiency of about 60%. Yttria-stabilised zirconia (YSZ) is used as the Oxygen ion conducting electrolyte in this fuel cell. It is a solid nonporous metal oxide (Solid zirconium oxide ZrO_2 to which a small amount of yttria Y_2O_3 is added). Ionic conduction by Oxygen ions takes place inside the fuel cell from cathode to anode to combine with Hydrogen to form water as shown in Fig. 6. The librated electrons flow to the cathode through the external circuit. At cathode, Oxygen atoms combine with electrons to generate more (O^-) ions to migrate to the anode across the electrolyte which permits only these ions to diffuse through it.
Reactions are as follows,

Anode: $H_2 + O^{--} \rightarrow H_2O + 2e^-$

Cathode: $\dfrac{1}{2}O_2 + 2e^- \rightarrow O^{--}$

Fuel cell: $H_2 + \dfrac{1}{2}O_2 \rightarrow H_2O + Energy$

Although high temperature enhances breakdown of cell components, it gives the flexibility to use more types of fuels and inexpensive catalysts. The SOFC provides several advantages compared to other fuel cell types. They generate few problems with electrolyte management (compared with liquid electrolytes, which are often corrosive and difficult to handle). Current technology employs several ceramic materials for the active fuel cell components. The standard material used for the cathode is a strontium doped lanthanum manganite (LaMnO$_3$). Material used for the anode is a mixture of nickel and yttria doped zirconia Ni-ZrO$_2$.

To generate a suitable voltage, fuel cells in the same stack are interconnected with a doped lanthanum chromate joining the anodes and cathodes of adjacent units. Although several stack designs are being considered around the world, the most common configuration is the planar (flat-plate) SOFC. Heat generated from this fuel at high temperature is a good option for cogeneration. However, cogeneration plants of 80% overall efficiency are already under development.

Direct Methanol Fuel Cell (DMFC)

The direct Methanol fuel cell is a new member in the PEMFC family, improved to operates directly with liquid Methanol CH_3OH, eliminating the need for fuel reformer. Initially DMFC's developed in the early 1990s, were not embraced because of their low efficiency, power density and other problems. If it can be made to work, that would be a big step forward in the automotive area. Prototypes exist, but the development is still at an early stage. There are principal problems, including the lower electrochemical activity of the Methanol as compared to Hydrogen, giving rise to lower cell voltage, and hence efficiency. Also, Methanol is miscible in water, so some of it is liable to cross the water-saturated membrane and cause corrosion and exhaust gas problems on the cathode side.

Improvements in catalysts and other recent developments [13-14] have increased power density up to 20 KW/m^3, and the efficiency may eventually reach 40%. The low operating temperature (50-120 C) and no requirement for onboard fuel reformer make the DMFC an excellent candidate for very small to mid-sized applications. Phones and other consumer products, up to automobile power plants are some examples. In modern cells, proton conducting polymer electrolyte membranes are often used, since these allow for convenient cell design and high temperature and pressure operation.

Figure 7. shows a schematic diagram and operating principles of the DMFC. At the anode, liquid Methanol (CH$_3$OH) is electrochemically oxidized to produce electrons which travel through the external circuit to the cathode. There, they are
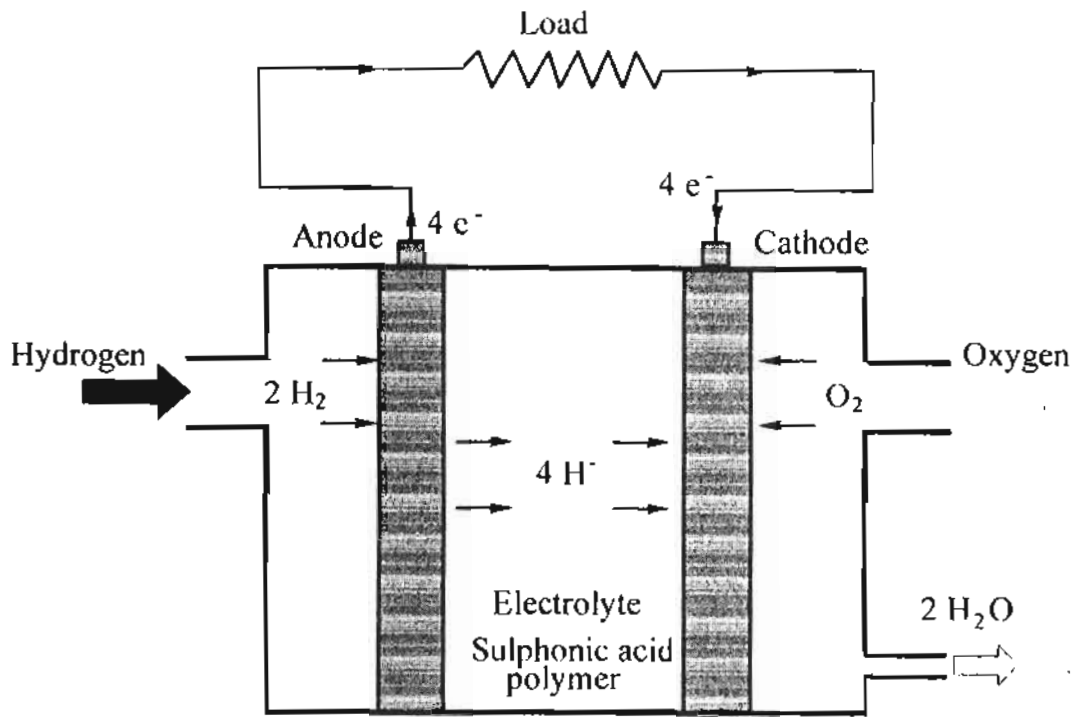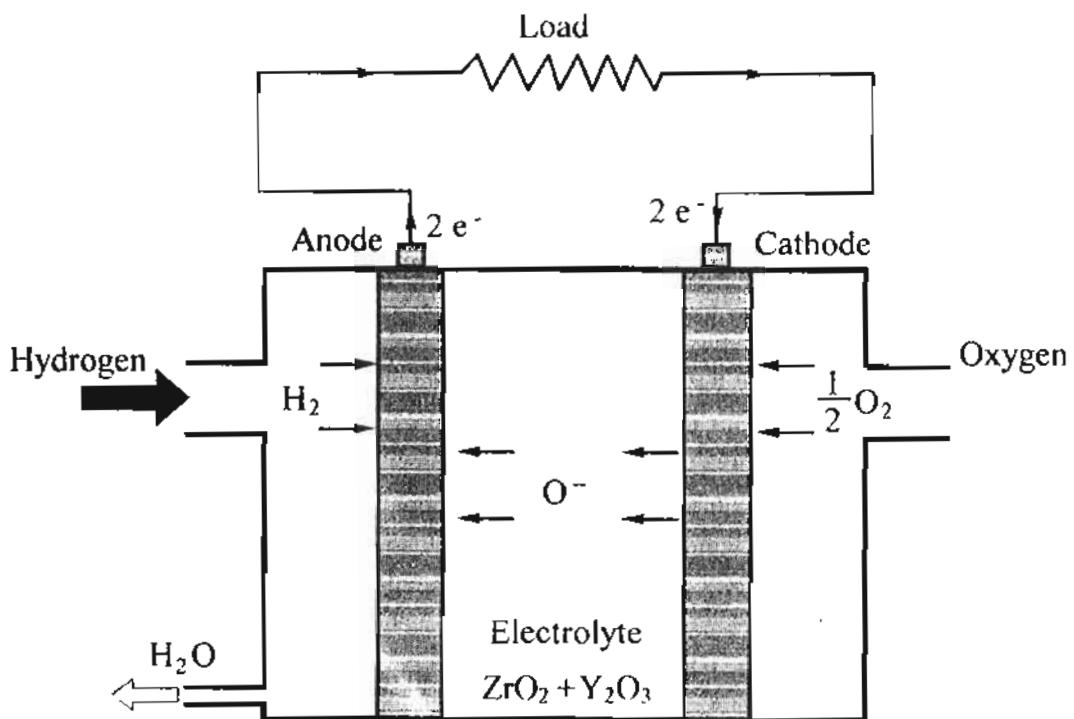
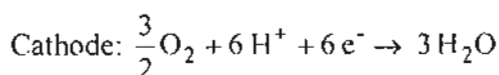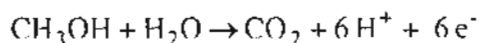Fig. 5. Proton exchange memberane fuel cell (PEMFC).

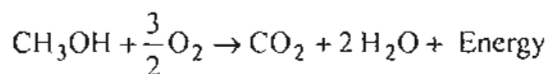Fig. 6. Solid oxide fuel cell (SOFC).

consumed together with Oxygen in a reduction reaction. The electric circuit is maintained within the cell by the conduction of protons in the electrolyte from anode to cathode.

Reactions are as follows.

Anode:

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$

Cathode: $\frac{3}{2}O_2 + 6H^+ + 6e^- \rightarrow 3H_2O$

Fuel cell:

$$CH_3OH + \frac{3}{2}O_2 \rightarrow CO_2 + 2H_2O + Energy$$

One of the drawbacks of the DMFC is that the low-temperature oxidation of Methanol to Hydrogen ions and Carbon dioxide requires a more active catalyst. Therefore, a larger quantity of expensive Platinum catalyst than that in conventional PEMFC is needed. This increased cost is, however, expected to be more than outweighed by the convenience of using a liquid fuel and the ability to function without a reforming unit. One other concern affecting the development of alcohol-based fuel cells is the fact that Methanol is toxic. Therefore, some companies have embarked on developing a direct Ethanol fuel cell (DEFC). The performance of the DEFC is currently about half that of the DMFC. But the gap between them is expected to narrow with further developments in DEFC.

Regenerative Fuel Cell (RFC)
This type of fuel cells is a new and attractive loop form of renewable power generation [15]. Water is separated into Hydrogen and Oxygen by a solar or wind-powered electrolysis process. Hydrogen and Oxygen are fed into the RFC fuel cell which generates electricity, heat and water. The water is then re-circulated back to the solar-powered electrolysis process and the cycle begins again. These types of fuel cells are currently being researched by NASA and others worldwide.

DISCUSSION
The above data are collected from many references and internet web sights [16]. Each fuel cell components, design, theory of operation, electrochemical reactions and technical limitations are systematically explained. The schematic diagrams are carried out in such a way to explain the theory of operation clearly, and fit exactly with the corresponding electrochemical reactions at electrodes. In some fuel cells, one of the products (water or Carbon dioxide) has to be re-circulated (partially or totally) from one electrode to the other. This fact is illustrated in the schematic diagram if exist. But the subject is still confusing because of the difference in fuel cell specifications and characteristics.

From the above, it can be seen that the fuel cell may have a liquid electrolyte (AFC, MCFC and PAFC) or a solid electrolyte (PEMFC and SOFC). The electrolyte may be acidic (PAFC and PEMFC) or alkaline (AFC, MCFC and SOFC). Fuel cells may differ in the catalyst material, operating temperature, efficiency and the other specifications. Therefore, the characteristics of the basic fuel cell types should be tabulated as shown in Table 1, and demonstrated graphically as shown in figures 8 and 9. By this way, it will be easy to compare between them and select the suitable fuel cell for a certain application. This also will be helpful in validating any new design.

As mentioned before, the electrolyte affects how hot the fuel cell runs and how susceptible it is to impurities in the fuel. In general, the hotter the fuel cell, the longer it takes to reach operating temperature and the more tolerance to impurities. The hottest running fuel cells are solid oxide and molten carbonate fuel cells. These types use either a solid ceramic or a liquid carbonate salt as their electrolytes. The high temperatures (650-1000 C) allow Oxygen to combine both with the Hydrogen and other impurities such as Carbon monoxide (CO) to form water and Carbon dioxide
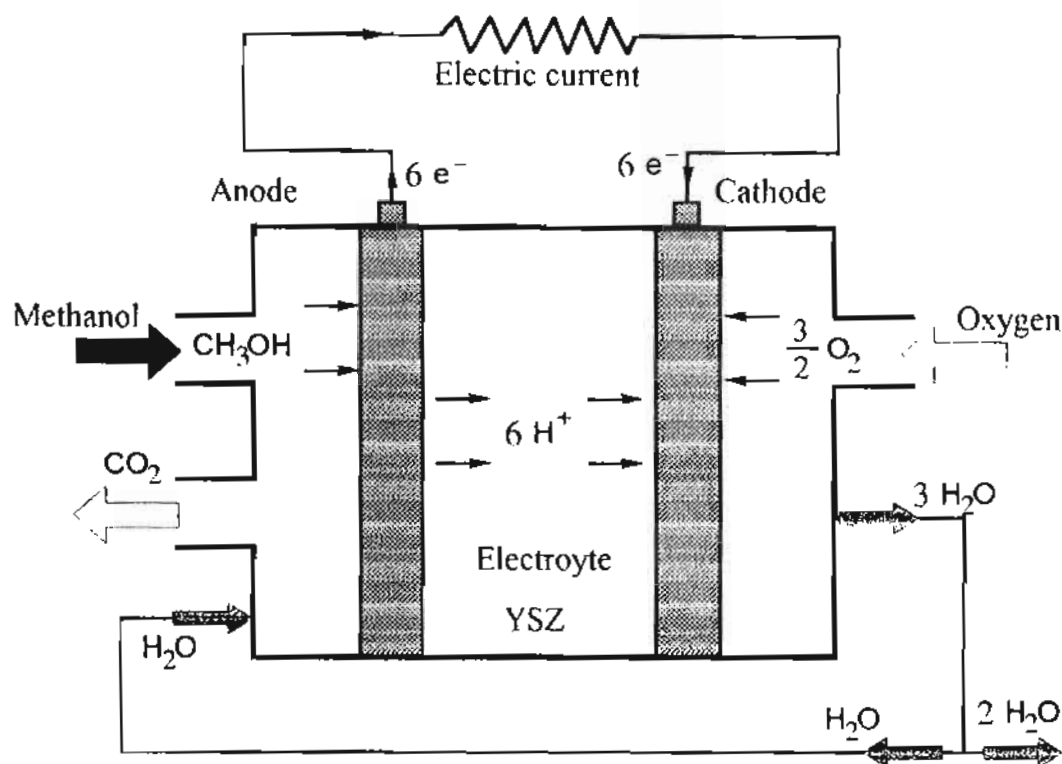
Fig. 7. The direct Methanol fuel cell (DMFC).

	AFC	MCFC	PAFC	PEMFC	SOFC
Electrolyte type	Alkali (KOH)	Alkaline (Li, Na & K) Carbonates	Phosphoric acid (Conc.)	Ion (Proton) Exchange Membrane	YSZ
Electrolyte state	Liquid	Liquid	Liquid	Porous solid	Solid
Ion type and sign	OH$^-$	CO$_3^-$	H$^+$	H$^+$	O$^-$
Operating temperature, C	80	650	200	80 - 100	1000
Fuel cell efficiency%	70	80	40-45	40 - 50	50-60
Cogeneration potential	None	High	Low Quality	None	High
Catalyst material	Platinum	Nickel	Platinum	Platinum	None
Electrolyte matrix	Asbestos	Stainless Steel	Silicon carbide	Carbon or Metal Based	Ceramic
Reformer	Yes	Yes - Non	Yes	Yes	Non
Power Generation	Small	Large	Large	Medium	Large
Vehicles	No	No	Yes	Yes	No
Space & defense	Yes	No	No	Yes	No

Table 1. Comparison between different types of fuel cells.

(CO_2) as products. These high temperature types of fuel cells don't have to be fed with pure Hydrogen. But they can run directly on natural gas or any hydrocarbon fuel. The fuel is broken down into Hydrogen and Carbon monoxide by the heat and the catalyst at the anode.

However, the cost to manufacture these high temperature devices is still very high; primarily because expensive alloys must be used to keep stable cell structures. These costs would be substantially reduced if the operating temperature could be lowered to 600-800 C. Therefore, cheaper structural components, such as stainless steel can be used. A lower operating temperature would also ensure greater overall system efficiency and a reduction in the thermal stresses in the active ceramic structures, leading to a longer expected lifetime. To reduce the operating temperature of SOFC, either the conductivity of YSZ is improved, or alternative electrolytic materials must be developed to replace it. A considerable effort is being made by researchers around the globe to develop such materials [12]. Ceramics that are currently being investigated include Gd-doped CeO_2, $Ba_2In_2O_5$ and (Sr,Mg)-doped $LaGaO_3$. However, these new materials face serious drawbacks compared with YSZ, and it is most likely that the first commercial SOFC units will use zirconia-based ceramics as the electrolyte.

On the other hand, the PAFC runs at 150 - 200 C and must be also supplied with Hydrogen, which does not have to be as pure as with the PEM type fuel cells. However, the higher temperature and lower efficiency makes it less desirable than PEM type fuel cells. Alkaline fuel cells AFC's are used in space missions and operate in a similar way to the PEM cells. But they are much larger for the same power output. PEM fuel cells have gained its popularity due to relatively low heat generation, high efficiency and clean operation. PEMFC's run at low temperatures (about 90°C), and for this reason cannot tolerate impurities in the Hydrogen fuel. The direct Methanol PEM fuel cell was developed as a solution to the high cost of extracting and purifying Hydrogen fuel. Methanol is cheaper to produce and can be easily made from plants. The DMFC cell runs slightly hotter (about 120 C) than the pure Hydrogen PEM cell, but produces Carbon dioxide and water as its byproducts.

Thermodynamic analysis

The fuel cell is a thermodynamic open system. The fuel and Oxygen (or air) flow in, while the products (water and Carbon dioxide) flow out. Energy (as electrical power and heat) flows out of the fuel cell (system) boundaries. Applying the first law of thermodynamics on the system yields,

$$FCE = IV + Q$$

Where, FCE is the fuel chemical energy,
   I the electric current,
   V the voltage drop across the load,
and   Q is the total generated heat.

If the operating temperature of the fuel cell is high enough (such in case of MCFC and SOFC), the total generated heat, Q can be extracted through a heat exchanger to supply a steam or a gas turbine to generate more power. For medium operating temperature fuel cells such as PAFC, the heat Q can be used in heating or industrial processes. Otherwise, it must be rejected by cooling to maintain a constant and stable operating temperature for the fuel cell. The heat rejected with water and Carbon dioxide at low temperatures can be considered as heat losses, Q_L. Therefore, the cell cogeneration efficiency, η_{co} is a more convenience measure for the fuel cell performance (in case of high temperature fuel cells MCFC and SOFC) other than the electrical efficiency η_e, where,

$$\eta_{co} = \frac{IV + Q_u}{FCE} = 1 - \frac{Q_L}{FCE}$$

$$\eta_e = \frac{IV}{FCE}$$

where, Q_u is the useful heat = $Q - Q_L$.

The fuel chemical energy (FCE) is simply the enthalpy of combustion calculated at the operating temperature. The standard value of enthalpy of combustion can be easily obtained from the fuel thermodynamic data as shown in Table 2. It is clear that the fuel cell cogeneration efficiency, η_{co} depends on the operating temperature, as will as the load (IV) as seen from the above equation.

A detailed analysis of the process can be obtained as follows,

If in a certain fuel cell, one mole (in grams) of Hydrogen and a half-mole of Oxygen from their normal diatomic forms combine to produces one mole of water. Work is provided to combine atoms and to decrease the volume of gases. Both of those are included in the enthalpy change. If this process is presumed at 25 C and standard atmospheric pressure, the work done on the system, W is given by, (see Table 2)

$W = P\Delta V$

$= (1.013 \times 10^5)(1.5)(22.4 \times 10^{-3})(298/273)$

$= 3715 \text{ J} = 3.72 \text{ KJ}$

Since the enthalpy $H = U + PV$, the change in internal energy is then,

$\Delta U = \Delta H - P\Delta V = 285.83 \text{ KJ} - 3.72 \text{ KJ}$

$= 282.1 \text{ KJ}$

The entropy of the gases decreases in the process of combination, since the number of water moles is less than that of Hydrogen and Oxygen,

$\Delta S = (130.57 + 205.14/2) - 69.1 = 163.34 \text{ J/K}$

$T\Delta S = (298)(163.34) \times 10^{-3} = 48.7 \text{ KJ}$

Since the total entropy will not decrease in the reaction, the excess entropy in the amount $T\Delta S$ must be expelled to the environment as a heat at temperature T. The amount of energy per mole of Hydrogen which can be provided as electrical energy is the change in the Gibbs free energy ΔG,

$\Delta G = \Delta H - T\Delta S = 285.83 \text{ KJ} - 48.7 \text{ KJ}$

$= 237.13 \text{ KJ}$

For this ideal case, the fuel energy is converted into electrical energy at an efficiency of 237.1/285.8 x100% = 83%. This efficiency is far greater than the ideal efficiency of a heat engine which burns Hydrogen to generate power. Although real fuel cells do not approach that ideal efficiency, they are still much more efficient than any real power plant burning Hydrogen.

Comparing the fuel cell process to its reverse reaction, electrolysis of water, it is useful to treat the enthalpy change as the overall energy change. The Gibbs free energy is that actually must be supplied to drive a reaction, or that can be obtained from it. So in the electrolysis/fuel cell pair, where the enthalpy change is 285.8 kJ, an amount 237.13 kJ of energy must be added to drive the electrolysis and the heat from the environment $T\Delta S = 48.7$ KJ will be added to help the reaction. On the other hand, in the fuel cell, an amount of 237.133 KJ as electric energy is obtained, but 48.7 KJ has to be dumped to the atmosphere.

CONCLUSION

The fuel cell is a quiet, clean, and reliable power source. This paper discusses the fuel cell technology, theory of operation, and classification. The fuel cell suitability for stationary, mobile and portable power generation units is studied. Also, the paper discusses the technical limitations to be overcome to harness the full potential of the fuel cell as a revolution in the power generation fields. Comparison of fuel cell types is also carried out in a systematic way to enable quick search and selection, and help research work in Egypt. The effect of operating temperature on the performance of different fuel cells is discussed. New fuels and the effect of fuel purity on the fuel cell performance have been also discussed. The latest fuel cell technologies have been surveyed. The regenerative fuel cell is seen to be a suitable choice for countries which have abundant solar radiation like Egypt. The PEM fuel cells have many advantages and are seen to be very promising. The
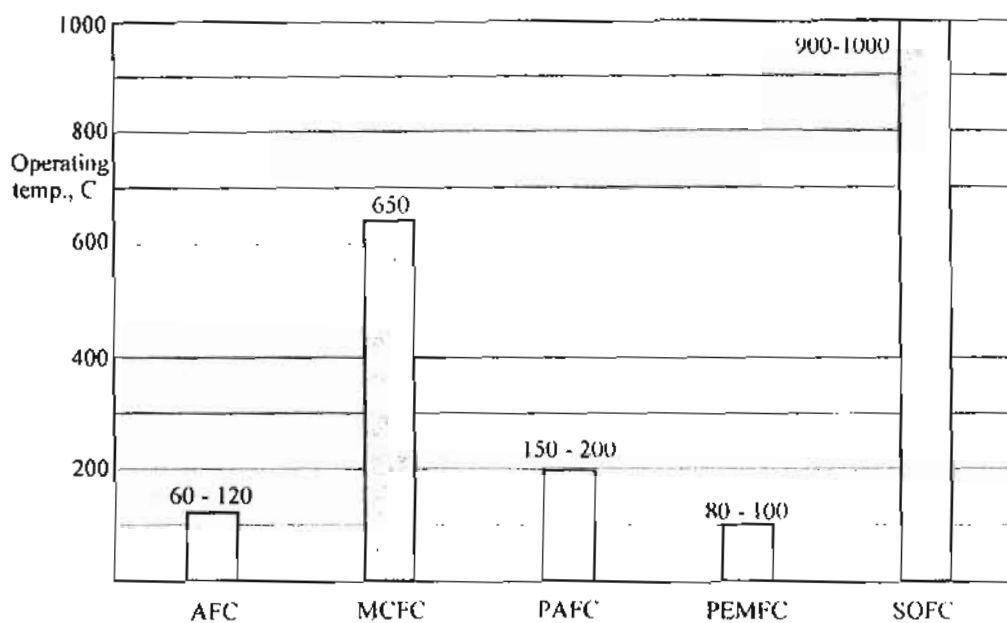
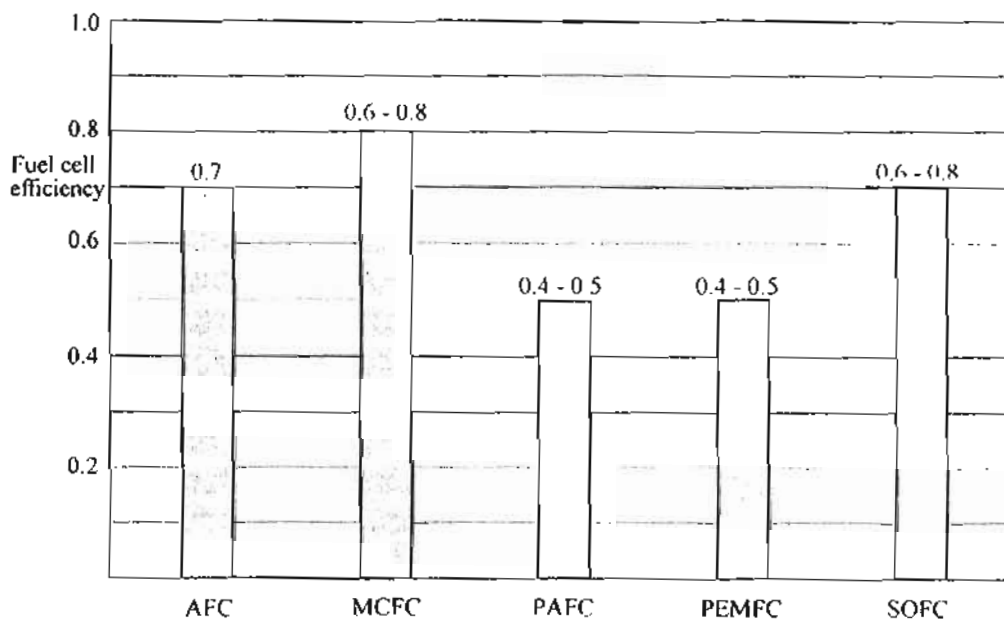Fig. 8. Graphical comparison between operating temperatures of fuel cells.

Fig. 9. Graphical comparison between different fuel cells efficiences.

Substance	Enthalpy ΔH (kJ)	Gibbs ΔG (kJ)	Entropy (J/ K)	Substance	Enthalpy ΔH (kJ)	Gibbs ΔG (kJ)	Entropy (J/ K)
CH_4 (g)	-74.81	-50.72	186.26	H (g)	217.97	203.25	114.71
C_2H_6 (g)	-84.68	-32.82	229.60	H_2O (g)	-241.82	-228.57	188.83
C_3H_8 (g)	-103.85	-23.49	269.91	Hg (l)	0	0	76.02
CO (g)	-110.53	-137.17	197.67	O_2 (g)	0	0	205.14
CO_2 (g)	-393.51	-394.36	213.74	O_2 (aq)	-11.7	16.4	110.9
H_2 (g)	0	0	130.68	OH^- (aq)	-229.99	-157.24	-10.75

Table 2. Thermodynamic properties of one mole at 20 C,
and standard atmospheric pressure. (g) : gas, (l) : liquid.

direct Methanol approach is attractive, but new methods have to be developed to deal with the produced Carbon dioxide. Other solutions being researched include efficient membranes with more tolerance to fuel impurities. Application of thermodynamic laws on the fuel cell performance has been discussed. A solved example is given to illustrate how to calculate the amount of energy which can be provided by the fuel cell per mole of Hydrogen. The calculated efficiency of the fuel cell in the example is seen to be greater than 80%. The paper concludes that fuel cells are almost ready, but the fuel to run them is holding them back. More researches are also needed for more cheap and reliable materials. This will of course encourage the researchers in the developing countries to give more efforts.

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