7 – Electrochemical conversion

1. Introduction

Some successive conversion processes are necessary to obtain electricity and heat from fossil resources. Three are the main stages: heat generation by fuel combustion, heat conversion into mechanical energy and power generation from mechanical energy. Boilers, turbines and electrical generators are the main equipments involved. Among these processes, the heat transformation into mechanical energy has the lowest efficiency. Besides the low efficiency, the processes based on the fossil fuels produce large emissions of CO_2 and solid waste, those long time accumulation in the environment are followed by serious climatic change.

Intensive research and development works were carried out to keep under control this dangerous evolution. New technologies for fossil fuel utilization were developed viewing those importance in the world energy consumption at least for the next decades. The main aimed improvements are increased efficiency and lower emissions.

Today, the renewable resources are of increasing importance to replace the fossil fuels. New conversion processes like photoelectric conversion of solar radiation, electrochemical conversion and thermo-electrical conversion are of major interest.

However, the most promising process remains the nuclear controlled fusion as a long term solution to meet the world energy demand.

2 Electrochemical conversion - Fuel Cell

A direct conversion of chemical energy of substances into electricity is possible through electrochemical reactions, without a thermodynamic stage. Some advantages arise in this case:

- large and expensive equipments like boiler, turbine, electrical generator and auxiliaries are removed;
- because the process temperature is constant, the conversion efficiency is no more limited by the thermo-dynamic laws. As consequence, a doubling of efficiency comparatively with the thermal power station is expected (until 80%).

The electrochemical energy conversion develops in the said „fuel cell”. This name comes from the fact that the primary energy source is a fuel, fossil like CH_4 or synthetic like hydrogen, methane, methanol, hydrazine etc. In a fuel cell these substances are submitted to oxidation and reduction reactions with secondary emissions similar to those of burning processes.

Operating principle

A fuel cell has two electrodes, separated by an electrolyte (fig.1).

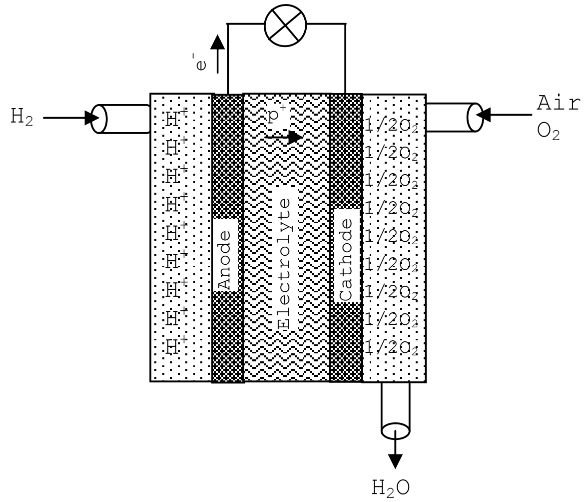

Fig.1 The $H_2 - O_2$ fuell cell

The anode, named „fuel electrode" is fed with H_2, which suffers an oxidation process, resulting protons and electrons.

The cathode, named „oxygen electrode" or „air electrode" is fed with atmospheric air or with oxygen. At cathode take place a reduction reaction of the molecular oxygen in the presence of protons transmitted via electrolyte.

The chemical reactions in the H_2-O_2 fuel cell, are:

- Anode $2H_2 \rightarrow 4H^+ + 4e^-$ (1)
- Cathode $4H^+ + O_2 + 4e^- \rightarrow 2H_2O$ (2)
- Global reaction $2H_2 + O_2 \rightarrow 2H_2O$ (3)

While the hydrogen ions (protons) pass through the electrolyte toward the cathode, the electrons flow by the electrical circuit under the influence of the electromotive force (voltage) arisen from the chemical reactions. This voltage represents the potential difference between the electrodes when an equilibrium exists with the electrolyte. The voltage is independent from the electrodes size and the internal impedance but depends on the electrodes structure and the electrolyte concentration.

The electromotive force

The overall equation of the energy balance for a fuel cell is:

$$\Sigma n_i U_i = zFE + Q + W \quad . \tag{4}$$

In equation (4):

- $\boldsymbol{n_i}$ represents the amount of substance ***i*** (number of mol). $\boldsymbol{n}>0$ if the substance ***i*** enter the reaction and $\boldsymbol{n<0}$ for the resulted substances;
- $\boldsymbol{U_i}$ represents the internal energy of the substance ***i***;

-***z*** is the number of electrons released by the oxidation reaction;
-***F*** = ***eN*** is the number of Faraday (where ***N*** =6,023.10 atoms/ mol) what represents the electrical charge of the electrons originating from a mol of substance;
-***E*** is the reaction electromotive force;
-***Q*** represents the released heat;
-***W*** is the mechanical work of the entered substances.

If released by the fuel cell, the energy quantities are negative but if enter the cell, they are positive. The volume of the residual product of the reaction may be neglected.

If the pressure and the temperature of the gases are known, the mechanical work can be written as:

$$W = - \Sigma p_i \ \Delta V_i \ = -\Sigma n_i \ p_i V_{\mu i} \qquad (5)$$

where:
- p_i is the partial pressure of the gas ***i***;
- n_i is the mol amount of the substance ***i***;
- $V_{\mu i}$ is the molar volume of the substance ***i***, having the reaction temperature ***T*** and pressure ***p***.

According to the second principle of the thermodynamics, all the irreversible energy conversion processes are associated with an entropy increasing

$$\Delta S \geq 0. \qquad (6)$$

For the ideal, theoretical reversible process corresponds the equality sign.

The entropy changes are:
-a growth arising from the chemical conversion

$$\Delta S_1 \ = - \ n_i \ S_i \ , \qquad (7)$$

where S_i is the entropy of a mol of the substance ***i***;
- a growth of the environment entropy

$$\Delta S_2 \ = Q/T \qquad (8)$$

owing to the released heat.

The electricity generation and the mechanical work consumption are free of entropy changes. So, results

$$\Delta S = \ \Delta S_1 + \Delta S_2 \ =- \ n_i \ S_i \ + Q/T \geq 0. \qquad (9)$$

By extracting the heat ***Q*** from the equation (4), results

$$Q = \ \Sigma n_i U_i \ - \ zFE - W. \qquad (10)$$

Introducing ***W*** from the equation (5):

$$-T\Sigma n_i S_i + \Sigma n_i U_i - zFE + \Sigma n_i p_i V_{\mu i} \geq 0$$

$$zFE \leq - T\Sigma n_i S_i + \Sigma n_i U_i + \Sigma n_i p_i V_{\mu i} \qquad (11)$$

$$zFE \leq \Sigma n_i \ (-TS_i + p_i V_{\mu i} + U_i)$$

The last equation can be written:

$$zFE \leq \ \Sigma n_i G_i \qquad (12)$$

where ***G = U + pV- TS*** is so-named free energy, introduced by Gibbs. Finally, the electromotive force becomes:

$$E \le \frac{\Delta G}{zF}. \qquad (13)$$

Equation (13) verifies even when the electrochemical reaction develops in the sense of energy storage (with consumption of electricity like for the case of batteries), but the equation sign changes.

Because the thermodynamic functions of the reaction depend on the temperature, the electromotive force depends on the temperature too. The actual potential difference between the electrodes differs from the theoretical value, owing to parasite reactions at the electrodes surface, others than the basic reactions. These parasite reactions reduce the cell voltage and provoke supplementary substances consumption so must be eliminated or slowed down, at least.

When the fuel cell operates connected to a consumer, the delivered voltage decreases because the voltage drop on the internal impedance and owing to the polarization processes on the electrode surfaces:

$$U = E - rI - \Sigma\Delta U \qquad (14)$$

Polarization manifests in three forms: electrochemical, chemical, concentration.

The ***electrochemical polarization*** represents the slowing down of the reaction at electrodes, what depends on the reaction form and the electrode structure. The reduction of this phenomenon can be possible using better catalysts, growing the active surface, increasing the temperature and the substances concentration.

The ***concentration polarization*** results from the slowing down access of the substances in the reaction area as well as the evacuation velocity of the residual product. Its effect can be reduces using porous electrodes.

The ***chemical polarization*** is induced by the low velocity of the reactions on the electrodes.

All polarization processes intensify if the current density growth, the temperature decreases and the reactants concentration decrease too. On the external V-A diagram of a fuel cell, three zones can be observed (fig.2):

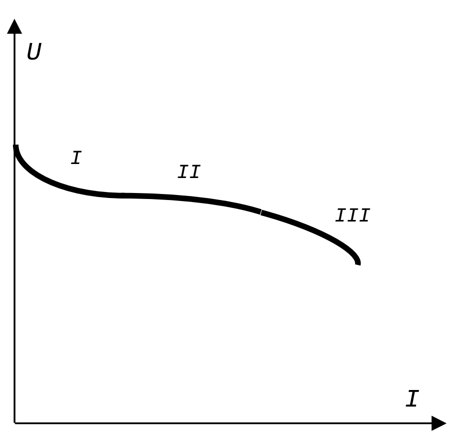

Fig.2 The output characteristic of the fuel cell

- zone I, where the electrochemical polarization has the main effect;
- zone II, where the internal voltage drop and the electrochemical polarization act together;
- zone III, where the voltage decreases faster owing to the chemical and concentration polarization.

Operation parameters of the fuel cell

The ***specific delivered energy*** represents the total electricity generated related to the mass of consumed fuel in the same period:

$$W = \frac{qE}{m} \qquad (15)$$

where:
q is the electrical charge issued in the reaction;
E is the electromotive force;
m is the consumed fuel mass.

For 1 mol of substance
q = zF,
so, for the „***m***” quantity, ***q*** becomes

$$q = zF\frac{m}{M}$$

where ***M*** is the mass for 1 mol of fuel.

Results

$$W = \frac{zFE}{M} \qquad (15)$$

Finally, considering the limit situation ***zFE = ΔG:***

$$W = \frac{\Delta G}{M} \quad (\mathrm{J/kg}). \qquad (16)$$

But for an accurate evaluation of the fuel cell performances, the entire cell mass must be considered, not only fuel mass. The obtained value ***W*** from the equation (16) must be multiplied with the proportion of the fuel mass to the cell mass. Also, the real voltage value must be considered instead of the theoretical value.

The *specific power* of a fuel cell can be different ways defined:

- related to the electrodes surface area

$$P_s = \frac{P}{S} = Uj \quad (\mathrm{W/m^2}) \qquad (17)$$

where ***j*** is the current density at the electrodes surface;

- related to the entire cell mass:

$$P_m = \frac{P}{M_p} \quad (\mathrm{W/kg});$$

- related to the cell volume

$$P_V = \frac{P}{V_p} \text{ (W/m}^3\text{)}.$$

The fuel cell efficiency

During a direct energy conversion process like that in the fuel cell, the process temperature remains constant, so the reaction enthalpy is converted into electricity, except an entropic quantity because of the released heat.

Using the formula of the free energy (Gibbs), the efficiency can be written:

$$\eta_{iz} = \frac{\Delta G}{\Delta H} = 1 - \frac{T\Delta S}{\Delta H} \qquad (18)$$

where $\boldsymbol{H = U + pV}$ represents the reactants enthalpy.

The efficiency can be higher than that of the conventional conversion process of the heat into electricity, limited by the second principle of thermodynamics. Actual performances of the fuel cell exceed 50% efficiency but a level of 80% is considered as possible in the future.

By selecting the reactants, becomes possible to reduce the released heat. Even a global endothermic reaction was realized with heat consumption from an external source. If that heat quantity originates as residual heat of other processes, the global conversion efficiency will be higher. Such a secondary source may be the cooling water of a power station.

Fuel cell technology

The electrodes

The electrodes structure and material are of first importance to obtain higher performances. In order to grow the energy density (Wh/kg), the electrodes must have a large active surface for the electrochemical reaction. Also, the nature of the surface has to accelerate these reactions. This demand is accomplished by catalytic elements, named in this case electro-catalysts.

The nature of utilized catalyst depends on the fuel nature and the operating conditions. For example, as the cell temperature higher is, the catalyst chemical activity may be lower because higher the temperature is, easier the level of activation energy may be overtaken by the reactants. For temperatures under 100^0C, the platinum is the best catalyst.

Besides the high chemical activity, the catalyst must have structural and chemical stability adequate to the operating temperature and to be inert related to the electrolyte.

A good electrode, must meet the next demands:

- structural stability in order to maintain the contact area between gases and electrolyte;
- a large contact area between gases and electrolyte in order to obtain higher current densities;

- good electrical conductivity to facilitate the electrons transfer towards the external circuit;
- good thermal conductivity to facilitate the transfer on released heat to the environment or cooling device.

The best qualities offer the pure or allied platinum. By economical reasons, other metals like palladium, iridium, gold, silver or nickel may be utilized too.

The electrolyte

The slowest stage of the electrochemical process is the transport of positive ions through the electrolyte. As consequence, a higher ionic conductibility of the electrolyte is necessary. The ideal situation is when all the positive ions reach the anode, without losses because of parasite reactions. From this point of view, an ions exchange membrane seems to be the ideal electrolyte.

The electrolyte nature has to be correlated with the operating temperature of the cell. For the cold cell, which operate at the room temperature, the electrolyte consists in water diluted acid or hydroxide solution.

For the warm cells, which operate at about 300^0 C, concentrated solutions or pure phosphoric acid or potassium hydroxide are used.

The hot cells, operate at $350\text{-}700^0$ C, so the electrolyte can be a molten carbonate. There are very hot fuel cells, which operate at temperature over 1000^0 C. For this case, the electrolyte is a ceramic solid.

The fuel

Viewing the high efficiency of electrochemical conversion, a major consequence could be a more advantageous utilization of fossil fuels. However, these substances present a too low reactivity to be possible a profitable operation of fuel cells. For now, is more efficient to use some substances resulted from chemical processing of natural fuels, as hydrogen, methanol, ammonia or synthetic substances as hydrazine.

Except hydrogen, the most interesting fuels are methanol and ammonia. The hydrazine is very expensive owing to the very low efficiency of its synthesis. However, the hydrazine has the highest reactivity than the other fuels of interest, being used for some applications like spatial or military devices.

Between methanol and ammonia, which are equal expensive, the first is preferred, because it’s higher reactivity.

Today, the majority of research and development works are focused on hydrogen as fuel.

According the fuel processing method, three types of fuel cell can be distinguished:

- ***direct fuel cell***, where the fuel is „burned” without a previous processing;

- ***indirect fuel cell***, when the fuel is chemically processed before enter the cell using an attached device to obtain hydrogen;
- ***regenerating cell***, where the fuel is obtained by processing the substance released by the cell using energy from other source, especially renewable. Thus, the fuel runs through a closed circuit so that the cell generates electricity by transforming the energy utilized to process the reaction output substance.

The regeneration process may use electric, thermal or radiating energy. If this energy is a residual output of other conversion process, the overall efficiency of conversion will be higher. Also, the fuel regeneration may be considered as an electricity indirect storage process.

Different types of fuel cells

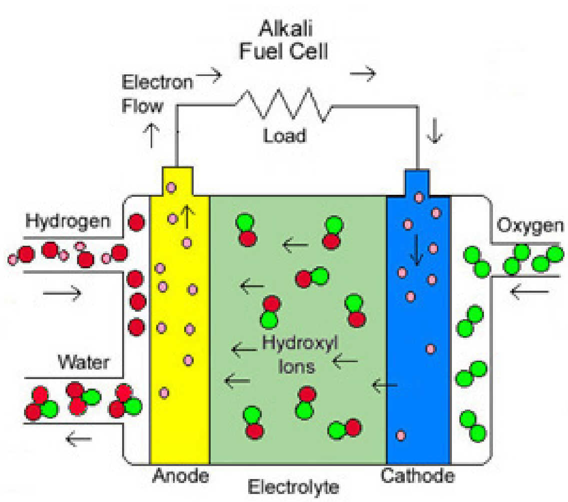

Fig.3 Drawing of an alkali cell

Alkali fuel cell (fig.3) operates on compressed hydrogen and oxygen. They generally use a solution of potassium hydroxide (chemically, KOH) in water as their electrolyte. Efficiency is about 70 percent, and operating temperature is 150 to 200 degrees C, (about 300 to 400 degrees F). Cell output ranges from 300 watts (W) to 5 kilowatts (kW). Alkali cells were used in Apollo spacecraft to provide both electricity and drinking water. They require pure hydrogen fuel, however, and their platinum electrode catalysts are expensive. And like any container filled with liquid, they can leak.

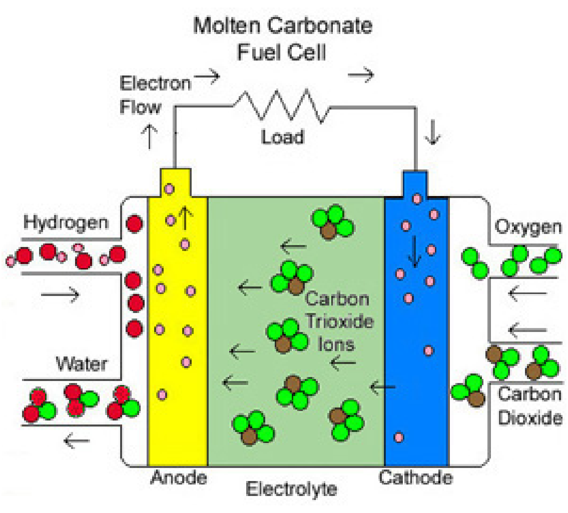

Fig. 4 Drawing of a molten carbonate cell

Molten Carbonate fuel cell (MCFC) (fig.4) uses high-temperature compounds of salt (like sodium or magnesium carbonates (chemically, CO_3) as the electrolyte. Efficiency ranges from 60 to 80 percent, and operating temperature is about 650^{0}C). Units with output up to 2 MW have been constructed, and designs exist for unit up to 100 MW. The high temperature limits damage from carbon monoxide "poisoning" of the cell and waste heat can be recycled to make additional electricity. Their nickel electrode-catalysts are inexpensive compared to the platinum used in other cells. But the high temperature also limits the materials and safe uses of MCFCs—they would probably be too hot for home use. Also, carbonate ions from the electrolyte are used up in the reactions, making it necessary to inject carbon dioxide to compensate.

Phosphoric Acid fuel cells (PAFC) (fig.5) use phosphoric acid as the electrolyte. Efficiency ranges from 40 to 80 percent, and operating temperature is between 150 to 200 degrees C. Existing phosphoric acid cells have outputs up to 200 kW, and 11 MW units have been tested. PAFCs tolerate a carbon monoxide concentration of about 1.5 percent, which broadens the choice of fuels they can use. If gasoline is used, the sulfur must be removed. Platinum electrode-catalysts are needed, and internal parts must be able to withstand the corrosive acid.

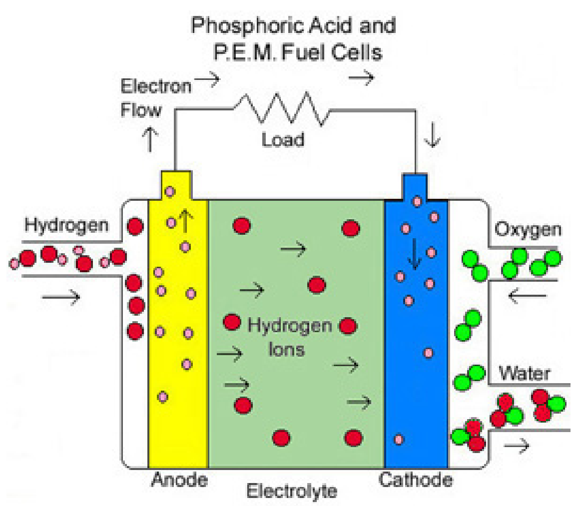

Fig. 5 Drawing of how both phosphoric and PEM fuel cells operate.

Proton Exchange Membrane (PEM) (fig.5) fuel cells work with a polymer electrolyte in the form of a thin, permeable sheet. Efficiency is about 40 to 50 percent, and operating temperature is about 80 degrees C. Cell outputs generally range from 50 to 250 kW. The solid, flexible electrolyte will not leak or crack and these cells operate at a low enough temperature to make them suitable for homes and cars. But their fuels must be purified, and a platinum catalyst is used on both sides of the membrane, raising costs.

Solid Oxide fuel cells (SOFC) (fig.6) use a hard, ceramic compound of metal (like calcium or zirconium) oxides (chemically, O_2) as electrolyte. Efficiency is about 60 percent, and operating temperatures are about 1,000 degrees C (about 1,800 degrees F). Cells output is up to 100 kW. At such high temperatures a reformer is not required to extract hydrogen from the fuel, and waste heat can be recycled to make additional electricity. However, the high temperature limits applications of SOFC units and they tend to be rather large. While solid electrolytes cannot leak, they can crack.

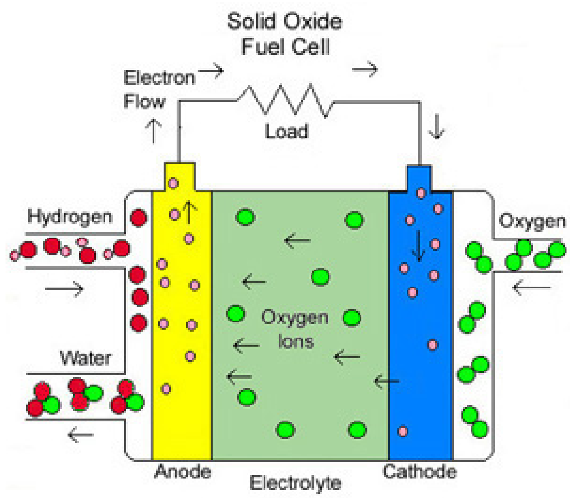

Fig. 6 Drawing of a solid oxide cell

The advantages of fuel cells - summary

- **High power efficiency**

The direct energy conversion in fuel cell reaches overall efficiency between 30% (for the beginning) and 90% (in the future), depending on its type and residual heat utilization. Because the cell operates at constant temperature, the second principle of thermodynamics limits the efficiency no more.

- **Low emissions**

If the fuel is hydrogen, electricity, heat and water are the reaction outputs. The heat can be recovered and water is a clean substance for the environment.

If fossil fuels like methane or oil are processed to obtain hydrogen, emissions of carbon dioxide, and sulphur oxide appear. However the emission level is lower by comparison with the generation of electricity from the same quantity of fuels.

- **Reduced environmental damages in mining areas**

The fuel cells utilization can reduce substantially the methane and oil extraction, if hydrogen is obtained using renewable sources of energy. This is a clear difference from the damages produced by drilling, transporting, storage and processing the fossil fuels.

- **Location**

Fuel cells may be located everywhere, inside or outside buildings, because they operate clean and noiseless.

- **Cogeneration**

If the residual heat of electrochemical reaction is recovered, it can be used for water heating, space heating or cooling. In this way, the overall efficiency reaches 90%.

- **Elastic operation**

To grow the electricity output, the fuel flow must be increased. The answer to charge change is similar with pushing the acceleration pedal of a vehicle.

- **Structural simplicity**

A fuel cell is a solid-state device. The lack of motion allows a simpler design, a higher reliability and noiseless operation.

- **Energy safety**

The necessary hydrogen for fuel cells may be obtained from various substances like coal, methane, oil, water, using renewable energy sources like sun and wind. The local generation of electricity and heat reduces the subordination to external oil and gas resources, which are mostly located in politically unstable areas.

Being the most abundant element in the universe, the feeding with hydrogen is practically endless. Starting the evolution to a hydrogen economy, the mankind can avoid a major energy crisis.

- **Independence from public networks**

A home energy system based on fuel cell allows the owner to be protected from the blackouts or power quality changes what can damage computers and other electric devices. If combined with other renewable energy conversion processes, the energy independence can be more complete.