New Materials for Emerging Energy Technologies

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1.Theme description

The European Commission since 2007 with the “Strategic Technology Plan” (Set-Plan) promotes the development of new technologies that allow to improve sustainability and efficiency, reducing costs. It can be achieved by coordinating the national research of European Countries and by financing projects.[1]

With Horizon 2020, EU gives the financial instrument to achieve these goals. Part of Horizon 2020 is the Leadership in Enabling and Industrial Technologies (LEIT)that supports the development of nanotechnologies, advanced materials, manufacturing and processing and biotechnology.[2]

In these context, the most promising energy technologies includes[3]:

- artificial photosynthesis;
- piezoelectric materials;
- thermoelectric structural power materials;
- low energy nuclear reactions.

The scopes of the innovative materials development is to reduce resources and energy consumption. Indeed, artificial photosynthesis could be used to produce energy from the sun without intermediate energy carriers(just a little part of 120

000 TW/year is use for mankind activities)[4]; thermoelectric generators could be used to convert waste heat into electricity (i.e. in the USA the amount of waste heat is about 36 TWh/year)[5].

In the following sections, the state of the art and the future trends of these technologies are described.

2.Technologies: State of Art and Future Perspectives

2.1 Artificial Photosynthesis

Artificial photosynthesis mimics the natural photosynthesis where chlorophyll uses sunlight to break down H_2O molecules into hydrogen, electrons and oxygen. Hydrogen and electrons convert CO_2 into carbohydrates, whereas the oxygen is expelled. In the artificial photosynthesis either oxygen and hydrogen could be produced. By this way, hydrogen could be used to produce energy, or to produce artificial fuels as methanol. The main problem of the process is splitting water molecules; the system need the use of catalysts like: manganese, titanium dioxide and cobalt oxide.[6]

Scientists are studying nanomaterials[7]and new processes[8]to improve efficiency. Today the artificial photosynthesis devices are not competitive with conventional energies equipment and tests are performed only in laboratory scale.

In the figures below two different devices are shown:

- Photo-electrochemical biofuel cell;
- Water splitting cell.

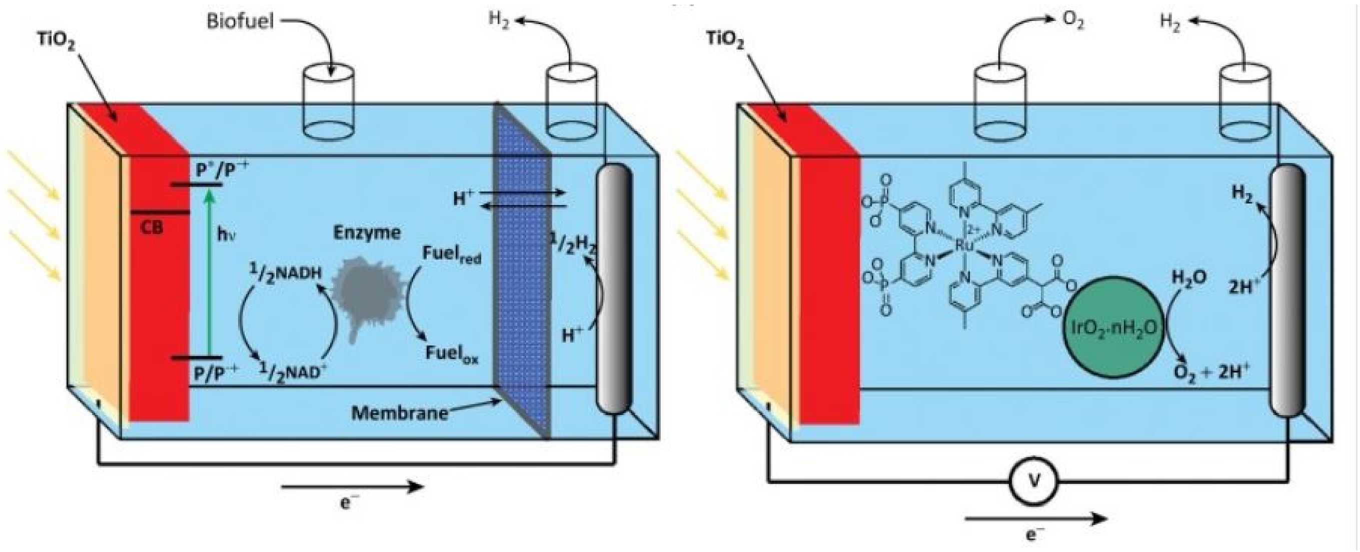


Figure 1 – a)Photoelectrochemical biofuel cell and b) Water splitting cell[5]

The first system uses sunlight to consume a biofuel (ethanol or methanol) and to generate hydrogen. The anode is a glass covered by a transparent conductor (indium tin oxide or fluorinated tin oxide) formed by a thin layer of nanoparticulate (tin dioxideor titanium dioxide). The electrode is immersed in an aqueous solution of NADH/NAD+. The energy absorbed generates electrons that flow through the cathode (i.e platinum electrode) immersed in the same solution, separated by means of membrane permeable to hydrogen's proton (H^+). Hydrogen or, if oxygen is present, electricity is produced. In the second system, the biofuel is substituted by an oxidant catalyst (IrO_2•nH2O) whereas the NADH solution is substituted by a ruthenium solution. The latter injects electrons on TiO_2. These electrons flow through the cathode where hydrogen's protons are reduced to hydrogen.

2.2 Piezoelectric Materials

Piezoelectric materials are widespread in our life. They are used in cars (fuel injection, airbag, parking sensors) in mobile phones (camera focus), at the hospital (microsurgery) in pressure sensors and transducers. When these materials are subjected to a mechanical stress they generate electric energy proportional to the stress. Vice versa when is applied an electrical field the piezoelectric produce a mechanical energy[9].

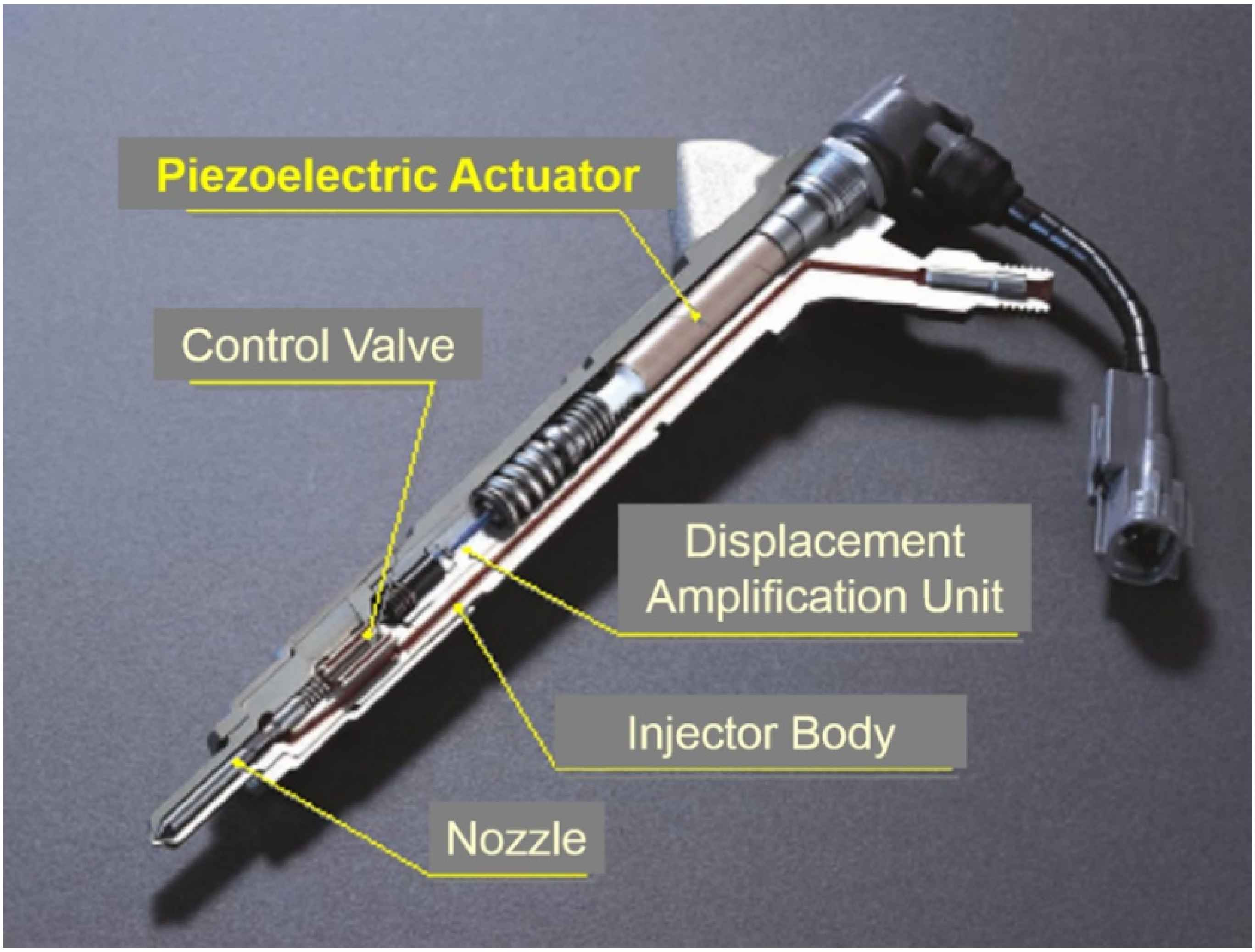


Figure 2 – Common rail injector[10]

Nowadays piezoelectric materials can be divided into three groups:

1. natural crystals (quartz);
2. ceramics (lead zirconate titanate, PZT);
3. polymers (polyvinylidene fluoride, PVDF).

Quartz has the highest quality factor (parameter that characterizes the sharpness of electromechanical resonance spectrum) suitable for loss transducers, whereas PZT has the highest electromechanical coupling factor (correspond to the rate of electromechanical transduction) and piezoelectric strain constant (measure the rate of strain due to an external electric field) suitable for high power transducer. PVDF has high voltage constant and mechanical flexibility, so it’s suitable for pressure/sensor applications[10].

The most used is the lead zirconate titanate ($Pb(Zr,Ti)O_3$) and the challenge is to find new materials because this alloy contains 60% in weight of lead (expensive material).[4]

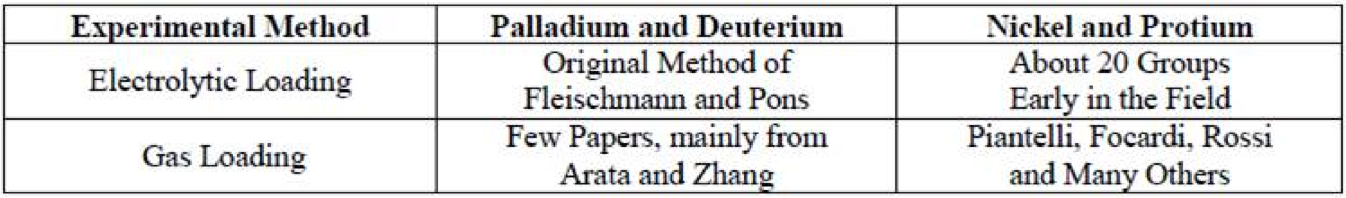
2.3 Low Energy Nuclear Reactions

In 1989, Stanley Pons and Martin Fleischmann demonstrated, in a small-scale laboratory, high release of heat, without radiation,by electrochemical charging of deuterium into palladium. This is called “cold fusion”. Nowadays cold fusion is included in the class of Low Energy Nuclear Reactions (LENR) and other materials have been found to produce the same effect(lithium and nickel).[11]

Instead of hot fusion, LERN necessities of solid materials and it doesn’t need a high flux of neutrons. The heat released is a function of deuterium concentration into palladium (this phenomenon is observed only if D/Pd> 0.9) hence a property metallurgy needs to be find.[4]A first nuclear reactor is under construction (ITER project[12])

The following table shows the main experiments and materials.

Electrochemical loading is mainly based on Pd/alloys with deuterons from heavy water because it is the system used in Fleischmann and Pons experiments. But, Ni/alloys with protons from hydrogen gas, are preferred for gas loading.



Experimental Method	Palladium and Deuterium	Nickel and Protium
Electrolytic Loading	Original Method of Fleischmann and Pons	About 20 Groups Early in the Field
Gas Loading	Few Papers, mainly from Arata and Zhang	Piantelli, Focardi, Rossi and Many Others

Table 1 – LERN experiments[13]

One of the most promising experiments is Rossi's E-Cat reactor. An external heat (electric or fossil) is applied in reaction chamber. The reactions begin when reactor temperature reached 60 °C and produce a large amount of heat (more than the energy input). This energy can be used to heat water and to produce steam. When the reaction is stable the external heat can be turned off and the reactions continue for hours.

The first plant (1MW$_{th}$) was tested in Bologna on October 28th, 2011. It ran for 5.5 hours producing 479 kW$_{e}$.

It is being tested small E-Cat reactors, 10-20 kW, for domestic market (Rossi's LeonardoCorporation).[14]

Figure 3 – 1MW_{th} E-Cat experimental apparatus[15]

2.4 Thermoelectric Generators

A thermoelectric system uses the Seebeck effect that allows to generate electrical power from a temperature gradient. The system consists of couples of semiconductors n-pconnected electrically in series and thermal in parallel. When a gradient temperature is applied, mobile electrons move from hot side (semiconductor n) to cold side (semiconductor p) where there are free holes. The net charge produces an electrostatic potential.

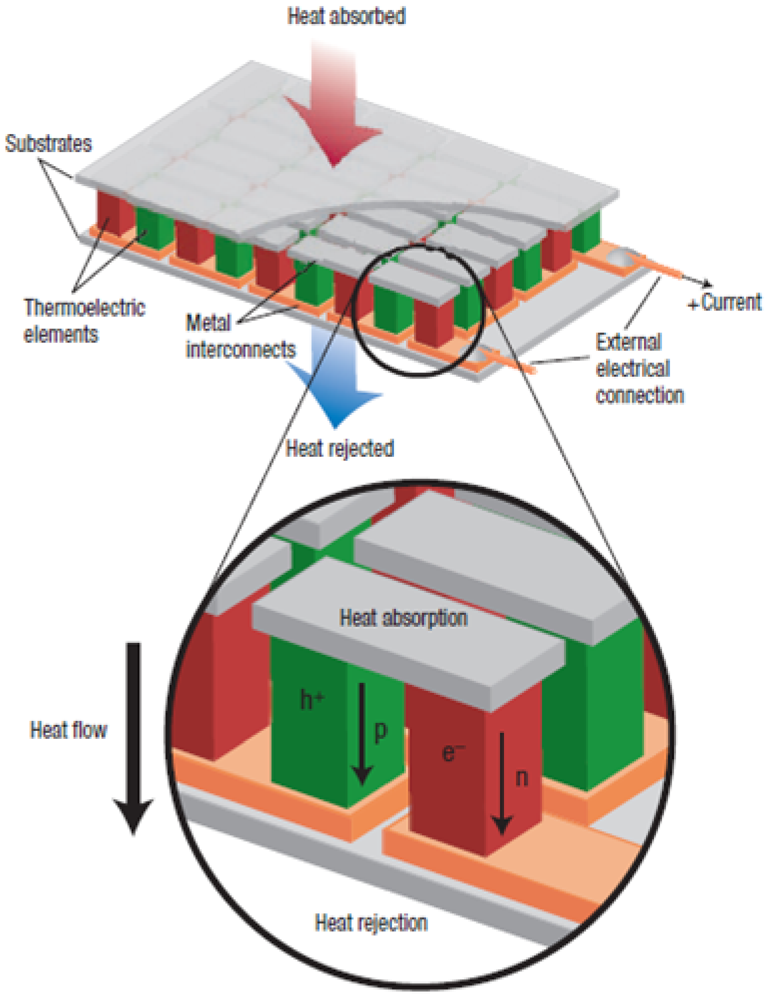


Figure 4 – Thermoelectric Generators[16]

The efficiency is estimated by means of a dimensionless group (figure of merit):

$$ZT = \frac{\alpha^2 \sigma}{k} T$$

- α = Seebeck coefficient;
- σ = electrical conductivity;
- k = thermal conductivity;
- T = absolute temperature.

Therefore, materials should have high Seebeck coefficient and electrical conductivity and small thermal conductivity.

Nowadays, materials used for this application are divided into three groups depending on the temperature[17]:

1. bismuth telluride (Bi_2Te_3) at low temperature (< 400 K);
2. lead telluride (PbTe) at middle temperature (600-900 K);
3. silicon germanium (SiGe) at high temperature (> 900 K).

In the figure is reported the history of thermoelectric materials from 1960 up to now. There are three different regions:

- ZT ~ 1 and efficiency reached 4-5%
- ZT ~1.7 by the introduction of nanostructures and efficiency of 11-15%
- ZT > 1.7 and efficiency near 15-20%.

The most useful between these materials is Bi_2Te_3 but this alloy is toxic for the environmental. For thisreason, alloys ofMg_2Si, $CoSb_3$, ZnSb,ZnO have been studied to find a new class of materials.[4]

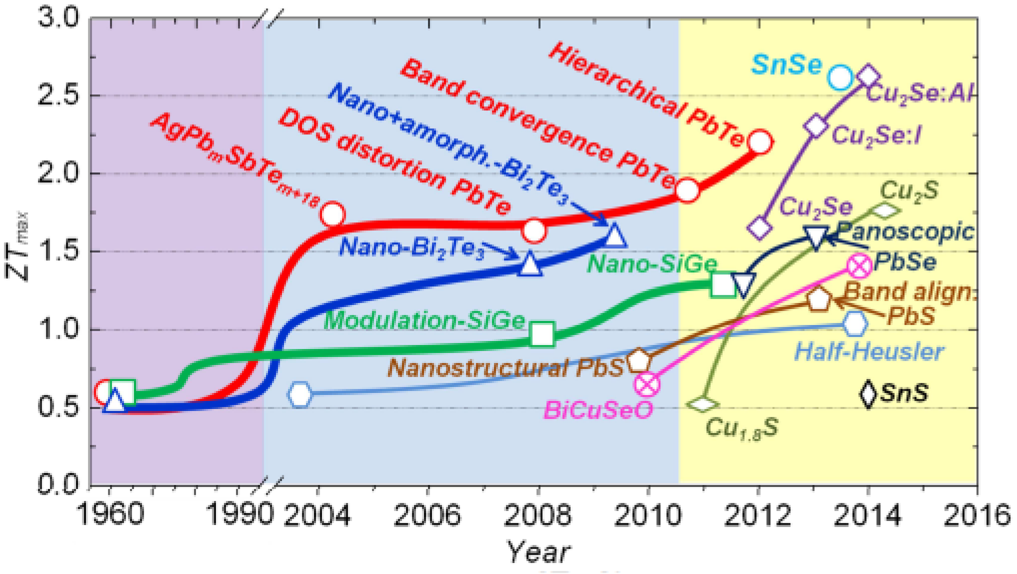


Figure 5 – History of thermoelectrical materials from 1960 to 2016[17]

3.Conclusions

These technologies are part of low-carbon energy technologies and are well within European “2050 Energy Strategy”. This strategic plan aims to reduce greenhouse gas emissions by 80-95% compared to 1990 levels, by 2050.[18]

Further R&D efforts need to be made on new materials that could allow their commercialization. Indeed, regarding to artificial photosynthesis innovative materials and low-cost fabrication technique are introduced (i.e.hydrothermal and chemical vapor deposition)[7]. However, the experimental tests are carried out on laboratory scale. Piezoelectric materials are widespread, but new alloys with less lead content are necessary. LERN’s experiments are difficult to reproduce, control and tests are related to few hours of continues operation. Thermoelectric materials have low efficiencies therefore new alloys are necessary to improve the figure of merit (ZT).

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