Thin film Si solar cell and solid oxide fuel cell technologies for a low cost, environmentally friendly and sustainable source of energy

Amine Boudghene Stambouli* and Samia Djerroud

Department of Electronics, Electrical and Electronics Engineering Faculty
University of Sciences and Technology of Oran
B.P. 1525, EL M’Naouer, Oran, Algeria.

(reçu le 17 février 2010 – accepté le 20 Juin 2011)

Abstract - Thin-film solar cell technology based on hydrogenated amorphous silicon has matured over the last two decades and is capable to deliver commercial modules with almost 10% stabilized efficiency. Moreover attention on hydrogen fuel cells is increasing as the range of potential commercial applications expands, with more than 3800 fuel cell systems being installed and operated worldwide. These systems attain high theoretical efficiencies in the range of 43.7-70.4 %, with an additional 20% as heat recovery, and operating at carbon-free conditions between 50 °C and 900 °C. In this paper the status of thin-film silicon solar cell technology is reviewed by comparing it to other major solar cell technologies. A discussion is also made upon the benefits obtained for potential applications, as long-term potential actions for sustainable development, and the future of Solid Oxide Fuel Cells (SOFCs). Applications of thin-film silicon modules and SOFCs are presented. EPIA (European Photovoltaic Industry Association) estimates that half of the growth in the next two years will come from thin-film technology.

Résumé - La technologie solaire des cellules couche mince à base de silicium amorphe hydrogéné a mûri au cours de ces deux dernières décennies et elle est capable actuellement d’offrir des modules commerciaux avec des efficacités stabilisées de près de 10 % En outre, l'attention sur les piles à combustible augmente à mesure que la gamme des applications commerciales potentielles se développe, avec plus de 3800 systèmes de piles à combustible installées et exploitées dans le monde entier. Ces systèmes atteignent des efficacités théoriques élevées de l'ordre de 43,7 à 70,4 %, avec un supplément de 20 % de récupération de chaleur, et de l'exploitation dans des conditions exemptes de carbone entre 50 °C et 900 °C. Dans cet article, l’état de la technologie solaire, des cellules au silicium à couche mince, est examiné par comparaison à d'autres grandes technologies de cellules solaires. Une discussion est faite sur les avantages obtenus pour des applications potentielles, comme c’est pour le cas des actions à long terme pour un développement durable, et sur l’avenir de piles à combustible à oxyde solide (SOFC). Les applications des modules de silicium couche mince et des piles à combustibles à oxyde solide sont présentées. L’EPIA (European Photovoltaic Industry Association) estime que la moitié de la croissance au cours des deux prochaines années proviendra de la technologie à couche mince.

Keywords: Solar cells - Thin Si films - Fuel cell - Solid oxide fuel cell – Hydrogen.

1. INTRODUCTION

In the last five years (2004 - 2009) the solar module production has grown on average 67 %, this means that the solar module market is one of the fastest growing
markets in the world. The total production of solar modules in 2009 exceeded 2 GWp \cite{1}. As shown in Table 1 and figure 1 solar cell technologies are dominated by bulk mono and multi-crystalline silicon (c-Si) solar cells, which accounted for 90.9 % of the total production \cite{1}.

As the c-Si solar cells, which represent the first generation solar cells for terrestrial applications, have matured, the cost of these solar cells has become dominated by material costs, namely those of the silicon wafer, the glass cover plate, and the encapsulants.

Depending on the location where the modules generate electricity, the price of the electricity that c-Si solar cells generate is still approximately three to five times higher, than the electricity from the traditional sources.

One way to decrease the cost of solar electricity is to reduce the thickness of the semiconductor materials that form a solar cell. There are several semiconductors that are excellent candidates for thin-film solar cells, such as silicon, copper indium gallium diselenide ‘CuInGaSe$_2$ = CIGS’ and cadmium telluride ‘CdTe’.

In comparison to bulk c-Si solar cells, in which the silicon wafer has a thickness of 300 micrometers, the total thickness of the semiconductor absorbers in thin-film solar cells is less than a few micrometers. An interesting development in the field of thin-film solar cells is the use of organic materials as light absorbers in solar cells. The best-known representative of these so-called organic solar cells is the dye-sensitized solar cell ‘DSC’, in which a monolayer of dye molecules is attached to a nanoporous TiO$_2$ thin film.

Low-cost thin-film solar cells are regarded as the second generation solar cells for terrestrial application. At present the price of electricity that solar modules based on thin-film solar cell technologies deliver is comparable to the bulk c-Si modules.

The potential of thin-film solar cells for a substantial cost reduction is expected to result from a large-scale production based on low-cost fabrication processes. In addition, the possibility of a cost effective integration of thin-film solar modules in all kinds of applications is also regarded as a major advantage.

Among thin-film solar cells, silicon has dominated the solar module market with 10.4 % of the total production, while the share of CIS and CdTe solar cells amounted to less than 3.5 % \cite{1}. At present the commercial thin-film silicon solar cells are represented by hydrogenated amorphous silicon ‘a-Si:H’ based solar cells.

A distinct feature of these solar cells is that silicon based layers are deposited in the low-temperature regime (T < 600 °C) by plasma assisted chemical vapour deposition techniques. Since in silicon solar cell technology the term thin-film usually covers a range of 1 to 100 micrometers thick layers, in this article thin-film silicon solar cells refer to the low temperature a-Si:H based solar cells.

<table>
<thead>
<tr>
<th>Technology</th>
<th>US</th>
<th>Japan</th>
<th>Europe</th>
<th>ROW</th>
<th>Total</th>
<th>Share</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-single-crystal</td>
<td>375</td>
<td>371.6</td>
<td>375.8</td>
<td>202.6</td>
<td>1325</td>
<td>33.5%</td>
</tr>
<tr>
<td>Si-polycrystallin</td>
<td>369.2</td>
<td>618</td>
<td>803</td>
<td>286.8</td>
<td>2077</td>
<td>52.5%</td>
</tr>
<tr>
<td>Si-single/polycrys. total</td>
<td>744.2</td>
<td>989.6</td>
<td>1178.8</td>
<td>489.4</td>
<td>3402</td>
<td>86%</td>
</tr>
<tr>
<td>a-Si:H outside</td>
<td>38</td>
<td>55</td>
<td>102.7</td>
<td>19</td>
<td>214.7</td>
<td>5.4%</td>
</tr>
<tr>
<td>a-Si:H inside</td>
<td>--</td>
<td>19.5</td>
<td>--</td>
<td>19.5</td>
<td>--</td>
<td>0.5%</td>
</tr>
<tr>
<td>a-Si:H total</td>
<td>38</td>
<td>74.5</td>
<td>102.7</td>
<td>19</td>
<td>234.2</td>
<td>5.9%</td>
</tr>
</tbody>
</table>

Table 1: Photovoltaic’s technology growth production in MW ‘2008’
It is well known that hydrogen is often hailed as the abundant and pollution-free power sources for the future. This would come from dissociating water into its component hydrogen and oxygen atoms using electrical energy or solar energy.

This fuel is proposed as a raw material for many applications, such as the production of useful electrical power, and can be considered as an appropriate global solution for the energy problem. Furthermore, hydrogen has a significant influence to the decrease of the environmental pollution, mainly due to its high impact on the world environmental health by limiting CO, CO₂, SO₂, NOₓ effluent gas emissions and global warming. Hydrogen is a superb fuel, theoretically locking up some 33000 Watt hours per kilogram.

Renewable and new energy holds the key to future prosperity and a healthy global environment and hydrogen Fuel Cells (FC) are considered as a promising way to solve the problem of intermittency that plagues electricity generation from renewable sources such wind and solar.

Based on a thermodynamic and economic analysis, hydrogen Fuel Cells are considered as an alternative source with suitable characteristics for electricity and heat cogeneration.

Solid oxide fuel cell (SOFC) systems, particularly, have grown in recognition as a viable fuel cell technology able to convert chemical energy into electricity and heat with high theoretical efficiencies in the range of 83.7-93.4 % unattainable from all conventional generator candidates such as gas-electric, micro-turbine and diesel-electric means.
Operating at carbon-free conditions between 650 and 900 °C, SOFCs offer a very significant ecological dimension in the problem of effective energy conversion.

2. SHORT OVERVIEW OF THIN FILM SILICON SOLAR CELL TECHNOLOGY DEVELOPMENT

Several attractive features are associated with a-Si:H material, which initiated the enormous interest in this material and made it a promising candidate for low-cost thin-film solar cells. Due to a high absorption coefficient in the visible range of the solar spectrum, a layer of a-Si:H less than 1 micrometer thick is sufficient to absorb 90% of usable solar light energy.

Using the plasma enhanced chemical vapour deposition (PECVD) technique thin films of a-Si:H can be deposited over a large area and at temperatures between 100°C and 400°C. Low processing temperature allows using a wide range of low-cost substrates such as glass sheet, metal or polymer foil.

Doping and alloying of a-Si:H is simply accomplished by adding the appropriate gases to a source gas, which is usually silane [2].

Research has concentrated, by the year 2000, on understanding and improving light trapping techniques, where surface textures as well as new transparent conductor oxide (TCO) materials play a crucial role.

This activity has resulted in the commercialisation of novel deposition techniques for ZnO as an alternative TCO material for SnO₂ [3, 4]. Several deposition machine manufacturers have started developing commercial production machines for the fabrication of thin-film silicon solar cells [5, 6].

Today’s the most advanced a-Si:H and μc-Si:H production lines are characterized by fully automated facilities, large area deposition over more than 1 m², with an annual production capacity in the range of 10 MWp to 30 MWp (Mitsubishi Heavy Ind. 10 MWp, Kaneka Corporation 20 MWp, United Solar 30 MWp).

3. STATUS OF THIN FILM SILICON SOLAR CELL TECHNOLOGY

Table 2 compares the present status of the thin-film Si solar cell technology with other major solar cell technologies [7, 8]. The best stabilized efficiency so far was demonstrated with a triple-junction a-Si:H/a-SiGe:H/a-SiGe:H solar cell structure of United Solar, which achieved 13 % on a laboratory cell with an area of 0.25 cm² and 10.4 % on a module level (~920 cm²) [7].

Recently, Kaneka Corporation has announced new results for the micromorph cell approach, an initial efficiency of 14.5 % for a tandem micromorph cell with the total area of 1 cm² and initial aperture efficiency of 12.5 % for a tandem micromorph module of 91 × 45.5 cm² [9].

The status of the thin-film Si solar cell technology on the module level is comparable to the other two main thin-film technologies, namely CIGS and CdTe. The encouraging results of Kaneka suggest that in near future commercial thin-film Si modules can achieve 10 % stabilized conversion efficiency.

The lower efficiency of thin-film Si relative to CIGS and CdTe at the cell level and the initial degradation of the performance when exposed to illumination are the present shortcomings of the thin-film Si solar cell technology.
Table 2: Performance status of the major solar cell technologies

<table>
<thead>
<tr>
<th>Technology</th>
<th>Thin-film solar cells</th>
<th>Bulk c-Si solar cell</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TF Si</td>
<td>CIGS</td>
</tr>
<tr>
<td>Efficiency %</td>
<td>9.3 single</td>
<td>18.9</td>
</tr>
<tr>
<td>(record cell)</td>
<td>12.4 tandem</td>
<td></td>
</tr>
<tr>
<td></td>
<td>13.0 triple</td>
<td></td>
</tr>
<tr>
<td>Efficiency %</td>
<td>10.4</td>
<td>12.1</td>
</tr>
<tr>
<td>(record module)</td>
<td>10.4</td>
<td>12.1</td>
</tr>
<tr>
<td>Efficiency %</td>
<td>5-9</td>
<td>9-11</td>
</tr>
<tr>
<td>(commercial module)</td>
<td>5-9</td>
<td>9-11</td>
</tr>
</tbody>
</table>

* Heterojunction with intrinsic thin layer

4. CURRENT TECHNOLOGY ISSUES

In order to increase the competitiveness of thin-film Si modules on the market, several cost- to-performance aspects of the thin-film Si solar cell technology are of importance, which can be divided into the following performance and production-related issues:

1. Increase of the conversion efficiency of thin-film Si solar cells which has to result from improved light management schemes such as light trapping and reduction of light absorption losses.

   For solar cells deposited on glass plates, also called superstrate-type cells, the development of a TCO front electrode material with an optimal surface morphology that results in improved light-scattering properties is essential.

   Essential for solar cells deposited on (flexible) opaque carriers, often denoted as substrate-type solar cells, is improvement of the texturing and reflectivity of the back contact.

   Ongoing attention has to be paid to further improvement of the opto-electronic quality of a-Si:H, a-SiGe:H, and μc-Si:H absorbers, the doped layers, and the interfaces between the doped layers and intrinsic absorbers.

2. Elimination of the light-induced degradation known as the Staebler-Wronski effect [10]. This effect is responsible for a decrease in the initial performance of an a-Si:H solar module of typically 15-30 %.

   Full understanding of the Staebler-Wronski effect in a-Si:H based materials is necessary for fabricating a-Si:H with improved stability against light exposure. The light-induced degradation of the modules can be suppressed by using thin absorber layers.

   However, the use of the thin absorbers strongly depends on the implementation of efficient light trapping techniques in the solar cells, which have to provide for sufficient absorption in these layers.

3. The deposition rate of absorber layers is required to be 10 to 20 Å/s in order to limit the investment in a thin-film Si deposition machine, which is strongly reflected in the cost of the modules. The central question regarding the deposition rate is how to avoid the increased light-induced degradation of films deposited at elevated deposition rates [11].
In addition to the rf PECVD technique, several deposition techniques are being intensively investigated capable of fabricating absorber layers with sufficient quality at high deposition rates, such as very high frequency PECVD, hot-wire CVD, and expanding thermal plasma CVD [12].

4. The choice of mass-production technology. Although the deposition of Si based absorber layers is the most important part of solar cell fabrication, complete production includes several fabrication steps which substantially contribute to the total cost of the solar module.

These include the deposition of the TCO front electrode, the deposition of the multi-layer back electrode, laser scribing for the sub-cell series connection, and encapsulation and framing. The solar cell structure and module design determine the choice of sequence of fabrication steps and the deposition and processing techniques to be applied. At present, there are three major approaches to depositing Si based layers:

The one-chamber batch process, the multi-chamber process, and the roll-to-roll process. The advantages and disadvantages of particular thin-film Si production systems are discussed in reference [12]. The general trend is to increase the substrate size, which reduces the cost per unit area, by lowering the relative contribution of the edges.

The experience gained in the display industry regarding the deposition of $a$-Si:H on large area substrates is transferred to solar cell production. The general requirements for the production machines include sufficient reliability of the deposition process, high production uptime, high yield, and the right choice of procedure for cleaning the process chambers.

5. Lowering of material costs. The material costs contribute considerably to the overall cost of thin-film Si modules. A substantial part is formed by the cost of the substrate carrier, the glass plate or high-temperature-resistant plastic foil.

Therefore, cheaper thin metal foils that also allow the use of the continuous roll-to-roll technology are a preferable choice. In case of flexible modules, usually a relatively thick fluoropolymer type encapsulant is applied in order to guarantee a module lifetime of 20 years.

The encapsulant dominates the cost of the module and the development of a cheap encapsulant is therefore one of the most important cost issues. The choice of substrate carrier determines the acceptable process temperatures and the sequence of processing steps. The choice of gasses for the deposition of Si absorbers, their purity, and the gas utilisation also has financial consequences.

For example, the use of germane for multijunction solar cells with $a$-SiGe:H absorbers can substantially increase the material costs.

5. FUEL CELLS

A fuel cell is an energy conversion device that converts the chemical energy of a fuel gas directly to electrical energy and heat without the need for direct combustion as an intermediate step, giving much higher conversion efficiencies than conventional thermo mechanical methods. Therefore, extracting more electricity from the same amount of fuel.

The operating principles of fuel cells are similar to those of batteries, i.e., electrochemical combination of reactants to generate electricity, a combination made of
a gaseous fuel (hydrogen) and an oxidant gas (oxygen from the air) through electrodes and via an ion conducting electrolyte.

However, unlike a battery, a fuel cell does not run down or require recharging. Fuel cell, with no moving parts, operates quietly and without combustion as long as both fuel and oxidant are supplied to the electrodes and the influence it exerts on the surrounding environment is negligible.

5.1 Design and operation of the fuel cell

A fuel cell consists of two electrodes sandwiched around an electrolyte. Hydrogen fuel is fed into the anode of the fuel cell and oxygen, from the air, enters the cell through the cathode. The hydrogen, under the action of the catalyst, splits into protons (hydrogen ions) and electrons, which take different paths towards the cathode.

The proton passes through the electrolyte and the electron create a separate current that can be used before reaching the cathode, to be reunited with the hydrogen and oxygen to form a pure water molecule and in some varieties of cells a lot of heat raising efficiency to 90.4 % [13].

5.2 Types of fuel cells

Fuel cells are generally classified by the chemical characteristics of the electrolyte used as the ionic conductor in the cell, as summarised in Table 3.

<table>
<thead>
<tr>
<th>Types of fuel cell</th>
<th>Electrolyte</th>
<th>Operating T (°C)</th>
<th>Fuel</th>
<th>Oxidant</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline (AFC)</td>
<td>Potassium hydroxide</td>
<td>50-80</td>
<td>Pure hydrogen, or hydrazine</td>
<td>O₂/Air</td>
<td>50-55 %</td>
</tr>
<tr>
<td>Direct Methanol (DMFC)</td>
<td>Polymer</td>
<td>50-80</td>
<td>Pure hydrogen, or liquid methanol</td>
<td>O₂/Air</td>
<td>40-55 %</td>
</tr>
<tr>
<td>Phosphoric Acid (PAFC)</td>
<td>Phosphoric Acid</td>
<td>150-200</td>
<td>Hydrogen from hydrocarbons and alcohol</td>
<td>O₂/Air</td>
<td>40-50 %</td>
</tr>
<tr>
<td>Sulfuric Acid (SAFC)</td>
<td>Sulfuric acid</td>
<td>80-90</td>
<td>Alcohol or impure hydrogen</td>
<td>O₂/Air</td>
<td>40-50 %</td>
</tr>
<tr>
<td>Proton-Exchange Membrane (PEMFC)</td>
<td>Polymer, proton exchange membrane</td>
<td>50-80</td>
<td>Less pure hydrogen from hydrocarbons or methanol</td>
<td>O₂/Air</td>
<td>40-50 %</td>
</tr>
<tr>
<td>Molten Carbonate (MCFC)</td>
<td>Molten salt such as nitrate, sulphate, carbonates</td>
<td>630-650</td>
<td>Hydrogen, carbon monoxide, natural gas, propane, marine diesel</td>
<td>CO₂/O₂/Air</td>
<td>50-60 %</td>
</tr>
<tr>
<td>Solid Oxyde (SOFC)</td>
<td>Ceramic as stabilised zirconia and doped perovskite</td>
<td>650-900</td>
<td>Hydrogen, natural gas or propane</td>
<td>O₂/Air</td>
<td>45-60 %</td>
</tr>
<tr>
<td>Protonic ceramic (PCFC)</td>
<td>Thin membrane of barium cerium oxide</td>
<td>600-700</td>
<td>Pure hydrogen and hydrocarbons</td>
<td>O₂/Air</td>
<td>45-60 %</td>
</tr>
</tbody>
</table>
A. Boudghene Stambouli et al.

<table>
<thead>
<tr>
<th></th>
<th>AFC</th>
<th>DMFC</th>
<th>PAFC</th>
<th>SAFC</th>
<th>PEMFC</th>
<th>MCFC</th>
<th>SOFC</th>
<th>PCFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power density (W/cm²)</td>
<td>0.2-0.35</td>
<td>0.04-0.23</td>
<td>0.2-0.25</td>
<td>0.2-0.3</td>
<td>0.35-0.36</td>
<td>0.1-0.2</td>
<td>0.24-0.3</td>
<td>0.2-0.3</td>
</tr>
<tr>
<td>Life time (kh)</td>
<td>10-15</td>
<td>10-15</td>
<td>40-60</td>
<td>20-35</td>
<td>40-65</td>
<td>40-65</td>
<td>40-80</td>
<td>40-70</td>
</tr>
<tr>
<td>Cost/price* (US$/kW)</td>
<td>200</td>
<td>200</td>
<td>1000</td>
<td>800</td>
<td>200</td>
<td>100</td>
<td>1500</td>
<td>1500</td>
</tr>
</tbody>
</table>

* Projected period 2010-2015

The type of electrolyte used dedicates their performance characteristics, making each type of fuel cell suitable for particular applications. There are also other types of fuel cells which are less employed but may later find a specific application.

Examples are the air depolarised cells, sodium amalgam cells, biochemical fuel cells, inorganic redox cells, regenerative cells, alkali metal-halogen cells, etc. Present materials science has made the fuel cells a reality in some specialised applications.

By far the greatest research interest throughout the world has focussed on Proton Exchange Membrane (PEM) and Solid Oxide (SO) cell stacks. PEMs are well advanced type of fuel cell that are suitable for cars and mass transportation. SOFC technology is the most demanding from a materials standpoint and is developed for its potential market competitiveness arising from:

• SOFC is the most efficient (fuel input to electricity output) fuel cell electricity generator currently being developed world-wide.
• SOFC is flexible in the choice of fuel such as carbon-based fuels and natural gas.
• SOFC offers the best potential for use with hydrocarbon –derived fuels.
• SOFC technology is most suited to applications in the distributed generation (i.e., stationary power) market because its high conversion efficiency provides the greatest benefit when fuel costs are higher due to long fuel delivery systems to customer premises.
• SOFC has a modular and solid state construction and do not present any moving parts, thereby are quiet enough to be installed indoors.
• The high operating temperature of SOFCs produces high quality heat by-product which can be used for co-generation or for use in combined cycle applications.
• SOFC do not contain noble metals that could be problematic in resource availability and price issue in high volume manufacture.
• SOFC do not have problems with electrolyte management (liquid electrolytes, for example).
• SOFC has extremely low emissions by eliminating the danger of carbon monoxide in exhaust gases, as any CO produced is converted to CO₂ at the high operating temperature.
• SOFC has a potential long life expectancy of more than 40000 to 80000 hrs.

### 6. SOLID OXIDE FUEL CELLS

SOFCs have recently emerged as a serious high temperature fuel cell technology.
They promise to be extremely useful in large, high-power applications such as full-scale industrial stations and large-scale electricity-generating stations. Some fuel cell developers see SOFCs being used in motor vehicles. A SOFC system usually utilizes a solid ceramic as the electrolyte and operates at extremely high temperatures (650 - 900 °C).

This high operating temperature allows internal reforming, promotes rapid electro catalysis with non-precious metals, and produces high quality by-product heat for co-generation. Efficiencies for this type of fuel cell can reach up to 60.4 % with an additional 20 % as heat recovery. SOFCs are best suited for provision of power in utility applications due to the significant time required to reach operating temperatures.

6.1 Design and operation of SOFCs

SOFCs differ in many respects from other fuel cell technologies. First, they are composed of all-solid-state materials. Second, the cells can operate at temperatures as high as 950 °C, significantly hotter than any other major category of fuel cell. Third, the solid state character of all SOFC components means that there is no fundamental restriction on the cell configuration.

A SOFC consists of two electrodes sandwiched around a hard ceramic electrolyte such as the remarkable ceramic material called zirconia. Hydrogen fuel is fed into the anode of the fuel cell and oxygen, from the air, enters the cell through the cathode. By burning fuel containing hydrogen on one side of the electrolyte, the concentration of oxygen is dramatically reduced.

The electrode on this surface will allow oxygen ions to leave the electrolyte and react with the fuel which is oxidised, thereby releasing electrons (e⁻). On the other side of the plate, which is exposed to air, an oxygen concentration gradient is created across the electrolyte, which attracts oxygen ions from the air side, or cathode, to the fuel side, or anode.

If there is an electrical connection between the cathode and the anode, this allows electrons to flow from the anode to the cathode, where a continuous supply of oxygen ions (O²⁻) for the electrolyte is maintained, and oxygen ions from cathode to anode, maintaining overall electrical charge balance, thereby generating useful electrical power from the combustion of the fuel. The only by-product of this process is a pure water molecule (H₂O) and heat, as shown in figure 2.
The major difference between the two types (a) and (b) is the side in the fuel cell in which the water is produced: the oxidant side in proton-conductor fuel cells and the fuel side in oxygen-ion-conductor ones.

The SOFC reactions include:

**Anode side**

\[
\begin{align*}
H_2 + O^{2-} & \rightarrow H_2O + 2e^- \\
CO + O^{2-} & \rightarrow CO_2 + 2e^- \\
CH_4 + 4O^{2-} & \rightarrow 2H_2O + CO_2 + 8e^- \quad \text{(fuel containing hydrogen)}
\end{align*}
\]

**Cathode side**

\[
O_2 + 4e^- \rightarrow 2O^{2-}
\]

### 6.2 Materials for cell components

The stability of the following SOFC components materials, over long periods, has been proven by a number of SOFC manufacturers and each component of serves several functions and must therefore meet certain requirements \[14\] such as proper stability, proper conductivity, chemical compatibility with other components, similar thermal expansion to avoid cracking during the cell operation, dense electrolyte to prevent gas mixing, porous anode and cathode to allow gas transport to the reaction sites, high strength and toughness properties, fabricability, amenable to particular fabrication conditions, compatibility at higher temperatures at which the ceramic structures are fabricated and low cost.

#### 6.2.1 Electrolyte

Although a variety of oxide combinations have been used for solid non-porous electrolytes, the most common to date has been the stabilised zirconia with conductivity based on oxygen ions (O$^{2-}$), especially yttria-stabilised zirconia (Y$_2$O$_3$ – stabilised ZrO$_2$ or YSZ, (ZrO$_2$)$_{0.92}$(Y$_2$O$_3$)$_{0.08}$ for example) in which a tiny amounts of the element yttrium, a silvery-grey metal, is added to the zirconia during manufacture. This choice is
mainly due to availability and cost (70% of the world’s supply of zirconia comes from Australia).

YSZ exhibits purely oxygen ionic conduction (with no electronic conduction). The crystalline array of ZrO₂ has two oxide ions to every zirconium ion. But in Y₂O₃ there are only 1.5 oxide ions to every yttrium ion. The result is vacancies in the crystal structure where oxide ions are missing. So, oxide ions from the cathode leap from hole to hole until they reach the anode. The most commonly used stabilising dopants are CaO, MgO, Y₂O₃, Sc₂O₃ and certain rare earth oxides such as Nd₂O₃, Sm₂O₃, Yb₂O₃.

Other oxide based ceramic electrolyte that can be used in SOFC (Fig. 3) [15] include:

- Cerium oxide doped with samarium (SDC), (Ce₀.₈₅Sm₀.₁₅)O₁.₉₂₅
- Cerium oxide doped with gadolinium (GDC), (Ce₀.₉₀Gd₀.₁₀)O₁.₉₅
- Cerium oxide doped with yttrium oped Ceria (YDC), (Ce₀.₈₅Y₀.₁₅)O₁.₉₂₅
- Cerium doped with calcium (CDC), (Ce₀.₈₈Ca₀.₁₂)O₁.₈₈
- Lanthanum gallate ceramic that include lanthanum strontium gallium magnesium (LSGM), (La₀.₈₀Sr₀.₂₀)(Ga₀.₉₀Mg₀.₁₀)O₂.₈₅ or (La₀.₈₀Sr₀.₂₀)(Ga₀.₈₀Mg₀.₂₀)O₂.₈₀
- Bismuth yttrium oxide (BYO), (Bi₀.₇₅Y₀.₂₅)₂O₃
- Barium Cerate (BCN), (Bi₀.₇₅Y₀.₂₅)₂O₃ and
- Strontium Cerate (SYC), Sr(Ce₀.₉₅Yb₀.₀₅)O₃

![Typical ionic conductivity of some electrolyte materials as a function of operating temperature](image)

6.2.2 Anode

Metals can be used as SOFC anode materials because of the reducing conditions of the fuel gas. Moreover, these metals must be non-oxidised since the composition of the fuel changes during the operation of the cell. SOFC anodes are fabricated from composite powder mixtures of electrolyte material and nickel oxide NiO (the nickel oxide subsequently being reduced to nickel metal prior to operation) [16], which serves to inhibit sintering of the metal particles and to provide a thermal expansion coefficient comparable to those of the other cell materials. The anode structure is fabricated with a porosity of 20 to 40% to facilitate mass transport of reactant and product gases.

6.2.3 Cathode

Because of the high operating temperature of the SOFC, only noble metals or electronic conducting oxide can be used as cathode materials. Noble metals are
unsuitable for practical applications because of their prohibitive cost and insufficient long thermal stability [17]. Several heterometallic oxides have been proposed and tested.

The choice of the electrode material depends on the target application, the specific ceramic electrolyte material, the desired operating temperature range, the electrochemical cell design, and the specific ceramic fabrication methods.

The most common applications for these materials are as cathode materials for solid oxide fuel cells and as electrode materials for oxygen generation systems. Perovskite-type lanthanum strontium manganite, LaSrMnO$_3$ (LSM) and lanthanum calcium manganite, LaCaMnO$_3$ (LCM) offer excellent thermal expansion match with zirconia electrolytes and provide good performance at operating temperatures above 800 ºC.

The incorporation of electrolyte material into the cathode material has been shown to improve electrode performance at lower temperatures by increasing the volume of active sites available for electrochemical reactions [18].

Similar to the anode, the cathode is a porous structure that must permit rapid mass transport of reactant and product gases.

6.2.4 Fuel

Fuels used just need to contain hydrogen but most contain carbon too, this fuel is reacted with oxygen from air, some fuel cells will need to reform the fuel if it is carbonaceous so that pure hydrogen is used but some will reform the fuel automatically. Hydrogen is obtained from electrically dissociating water molecules or from using solar cells which dissociate water molecules.

SOFCs require only a single partial oxidation reformer to pre-process its fuel, which can be gasoline, diesel, natural gas, etc. The nature of the emissions from the fuel cell will vary correspondingly with the fuel mix. Some sources that spring to mind are methane and methanol/ethanol, more complex hydrocarbons, such as pentane are now being used [18].

6.2.4.1 Hydrogen sources and production methods

There is a growing consensus that hydrogen has the potential to supplement and possibly replace fossil fuels for the production of energy by 2010-2020. Hydrogen can be produced from a wide range of source materials, including fossil fuels, biomass, some industrial chemical by-products and water via electrolysis.

The choice of source for a future hydrogen economy in worldwide, as elsewhere, would depend on various local factors including location of resources, available reserves, cost of extraction, cost of transportation and utilization.

The technique utilized to produce Hydrogen from the source will depend on technology development, required infrastructure investment, efficiency, location and suitability of local supplies.

Annual world production is currently around 5.4 $10^{11}$ Nm$^3$ corresponding 2 % of primary world energy demand [18]. Table 4 shows the principal production routes, indicating that 96% is produced from fossil fuels.

Table 4: Distribution of primary energy sources for world hydrogen production

<table>
<thead>
<tr>
<th>Primary source energy</th>
<th>SMR</th>
<th>OR</th>
<th>CG</th>
<th>E</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SMR</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>OR</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>CG</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>E</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Other</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.3 Cell geometries and stack configuration

The stack is the main component of the power section in a fuel cell power plant in which cell assemblies, each including an anode, electrolyte, and cathode, are stacked with interconnecting plates between them that connect the anode of one cell to the cathode of the next cell in the stack.

These plates are generally made of doped lanthanum chromite LaCrO$_3$, particularly suitable from its high electronic conductivity, its stability in the fuel cell environment and its compatibility with other cell components.

Plates are shaped to allow flow of the hydrogen and oxygen to the repeating unit. The cells are connected in electrical series to build a desired output voltage and can be configured in series, parallel, series-parallel or as single units, depending upon the type of applications.

The number of fuel cells in a stack determines the total voltage, and the surface of each cell gives the total current. Although several stack designs are being considered around the world (tubular, radial planar, planar, flat-plate, thin-film configurations design) the most common configuration is the planar (or ‘flat-plate’) SOFC, illustrated in figure 4, with its relative ease of manufacture and a lower ohmic resistance of the electrolyte, resulting in reduced energy losses.

However, no matter which design is employed; the fundamental electrochemical processes of cell operation remain the same.

![Fig. 4: Typical planar flat-plate SOFC configuration](image)

7. SOFCs AND THEIR ENVIRONMENTAL IMPACT

Issues of efficiency and ecology converge at this time to renew interest in SOFCs as systems for electricity generation. In recent times, they attract serious attention in the utility industries, particularly in co-generation of heat and power.

The environmental impact of SOFC use depends upon the source of hydrogen-rich fuel used. If pure hydrogen is used, fuel cells have virtually no emissions except water and heat. High efficiency of SOFC results in less fuel being consumed to produce a
given amount of electricity, which corresponds to lower emission of carbon dioxide CO2, the main 'greenhouse gas' responsible for global warming.

When hydrogen from natural gas is used as a fuel, SOFCs have no net emissions of CO2 because any carbon released is taken from the atmosphere by photosynthetic plants.

A reduction of carbon dioxide emissions by more than 2 million kg per year can be obtained [19]. Moreover, emissions from SOFC systems will be very low with near-zero levels of NOX, SOX and particulates, therefore eliminates 20000 kg of acid rain and smog-causing pollutants from the environment.

In any case SOFCs generally provide the lowest emissions of any non-renewable power generation method such as traditional thermal power plants, as shown in Table 5 [20]. This is very important regarding energy related environment concerns.

When combined with a heat engine that uses any waste heat, SOFCs are the most clean and efficient devices available for this purpose. SOFC can also provide high-quality waste heat that can be used to warm the home or provide refrigeration and air conditioning without harming the environment.

<table>
<thead>
<tr>
<th>Energy source</th>
<th>SOX (gSOx/kWh)</th>
<th>NOX (gNOx/kWh)</th>
<th>C in CO2 (gC2/kWh)</th>
<th>C in CO (gC/kWh)</th>
<th>Particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>3.400</td>
<td>1.8</td>
<td>322.8</td>
<td>40.0</td>
<td>0.00020</td>
</tr>
<tr>
<td>Oil</td>
<td>1.700</td>
<td>0.88</td>
<td>258.5</td>
<td>40.0</td>
<td>0.00015</td>
</tr>
<tr>
<td>Natural Gas</td>
<td>0.001</td>
<td>0.9</td>
<td>178.0</td>
<td>20.0</td>
<td>0.00002</td>
</tr>
<tr>
<td>Nuclear</td>
<td>0.030</td>
<td>0.003</td>
<td>7.8</td>
<td>7.8</td>
<td>0.00005</td>
</tr>
<tr>
<td>Photovoltaics</td>
<td>0.020</td>
<td>0.007</td>
<td>5.3</td>
<td>1.3</td>
<td>0</td>
</tr>
<tr>
<td>Fuel Cells</td>
<td>0</td>
<td>0</td>
<td>1.3</td>
<td>0.3</td>
<td>0</td>
</tr>
</tbody>
</table>

As mentioned earlier, hydrogen is rarely used due to problems with storage and transportation, but in the future many people have predicted the growth of a solar hydrogen economy.

8. BENEFITS AND APPLICATIONS OF THIN-FILM SI AND SOFCS TECHNOLOGIES

Due to the versatility of thin-film Si technology to produce rigid as well as flexible modules and the high energy yield, the application possibilities for thin-film Si modules are very broad.

A-Si:H modules have a substantially lower conversion efficiency temperature coefficient than crystalline silicon modules, which results in superior performance at higher operational temperatures.

This feature favours the implementation of a-Si:H modules in high-temperature conditions. The applications cover the following market areas:

- Consumer products where small solar cells provide electricity for calculators, watches. Small modules with power ranging from 3 to 50 Wp are used as (portable) battery chargers, in car roofs and a variety of other leisure products.
- Residential and commercial grid-connected systems that are mainly designed for Building-Integrated Photovoltaics (BIPV). The modules usually have a 20-year power
output warranty and can be structurally and aesthetically integrated as roofing or façade elements.

Taking advantage of the laser techniques that are applied during manufacturing of a-Si:H modules, partly transparent modules can be fabricated. Offering both environmentally friendly performance and a compelling design, these types of products open new possibilities in BIPV applications.

- Several large grid-connected systems have been realized with a-Si:H based modules. The largest array of flexible a-Si:H United Solar based modules was installed in California in 2003 to help power oil field operations (500 kWp installed power). The facility comprises 4800 flexible solar panels, each about 40 cm wide and 540 cm long, mounted on metal frames.

The world's largest amorphous silicon solar power plant (installed power of 1 MWp), employing Mitsubishi Heavy Ind. modules, was completed in the beginning of 2005 in the German city of Buttenwiesen in the suburbs of Munich. The power plant comprises approximately 10 000 amorphous silicon single-junction superstrate-type modules. The plant is annually expected to deliver 1 million kWh.

- Off-grid and remote-area applications include solar systems with a rated power of 30 to 50 Wp that are mainly designed for lighting in remote homes and construction sites without access to the power grid. Larger systems are designed to generate power for villages, remote homes, water pumping, telecommunications, traffic control signals, etc.

- Special applications. A candidate for space PV application.

Fuel cells in particular SOFCs have many advantages: they can be modular, they can be distributed to eliminate the need for transmission lines, and they operate quietly and are vibration free could provide higher system efficiency, higher power density, and simpler designs than fuel cells.

At low enough costs, they could compete with combined cycle gas turbines for distributed applications. The benefits of SOFCs also include: Energy security, Reliability, Low operating and maintenance cost and Constant power production.

![Graph showing fuel cells production](image)

**Fig. 5: Actuel and estimated world wide fuel cells production (Million of $US)**

SOFCs could be used in many applications. Each proposed use raises its own issues and challenges. Their most needed uses are:
• High power reliability: computer facilities, call centres, communication facilities, data processing centres high technology manufacturing facilities.
• Emission minimisation or elimination: urban areas, industrial facilities, airports, zones with strict emissions standards.
• Limited access to utility grid: rural or remote areas, maximum grid capacity.
• Biological waste gases are available: waste treatment plants, SOFC can convert waste gases (methanol from biomass) to electricity and heat with minimal environment intrusion.

Figure 5 illustrates the actual and estimated world demand on fuel cells [20].

8.1 Solar/hydrogen economy
In this scenario, photovoltaic cells would convert sunlight into electricity. This electricity would be used to split water (electrolysis) into hydrogen and oxygen, in order to store the sun's energy as hydrogen fuel.

SOFCs generating stations would have no real emissions of greenhouse or acid gases, or any other pollutants. Solar/fuel cells will allow the use of power from the sun twenty-four hours a day, and will provide an abundant, clean, efficient, locally produced source of energy as illustrated in figure 6.

![Fig. 6: Photovoltaic/Fuel Cells, the process](image)

The storage of hydrogen in this case is some kind of a headache. It is possible in liquid form, though this requires unwieldy and energy hungry cryogenic cooling; or as a gas pressurised at up to 10000 psi inside strong metal or composite cylinders.

The latter, highly engineered and regularly checked for safety, utilise a combination of material types and typically comprise a seamless metal liner with an over wrap of carbon fibre composite in which the fibres are aligned radially to provide high hoop strength.

Another possibility is to store the gas in the interstices of microporous media, such as carbon. Other materials, such as zeolites, are being investigated along with some hydrides, like those formed with iron/titanium, lanthanum/nickel, magnesium, magnesium/nickel and magnesium/titanium.
Recently Mazda Corporation in Japan has developed a palladium/magnesium alloy able to store 6.5 wt% of hydrogen at 100 °C and release the gas at 80 °C. Palladium used alone is known to have good hydrogen storage capability and capacity for frequent re-use [21].

9. CONCLUSION

Energy exploitation of fossil fuels is reaching its limits. Future alternatives must therefore be developed for long-term and environmental-friendly energy supply needed by a constantly growing world population.

The flexibility of a-Si:H solar cell technology to deliver modules for a large variety of applications is its most important asset. The technology has a strong potential to produce modules with an attractive cost-to-performance ratio generating electricity with a price competitive to that of conventional electricity.

The cost reduction of a-Si:H modules will be determined by the scaling rate of the production capacity, which does not rise as quickly as in case of the crystalline silicon solar cell technology.

At present, a-Si:H solar cell technology has to concentrate on solving several issues in order to become a fully mature technology.

Further development of thin-film silicon solar cell technology in general requires an increase in the performance of a-Si:H solar cells. One has to realize that two thirds of the power generated by a promising micromorph tandem (a-Si:H/μc-Si:H) solar cell comes from the a-Si:H top cell.

In the near future, attention will be paid to enhancing light trapping inside the cells, i.e. improving the TCO material quality and optimising the surface texture. At the same time, research will continue on a-Si:H based materials, which has recently resulted in a completely new class of nano-structured silicon films with a microstructure that exhibits crystalline domains imbedded in an amorphous network.

On the other hand, hydrogen fuel cells provide highly efficient, pollution free power generation. From the foregoing it is clear that new and improved materials have crucial role to play in fuel cell development. Indeed materials scientist may well hold the key to the hydrogen economy.

A new report unveiled recently by J. Barrett of the U.S. Economic Policy Institute (EPI) and J.A. Hoerner of the Centre for a Sustainable Economy (CSE), suggests that global warming can be reduced without harming the economy and that nobody needs to accept a choice between environmental degradation and economic calamity.

REFERENCES


