Innovative biomass fuelled SOFC’s for polygeneration

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Abstract

The supply of energy and the protection of the environment have been two of the most important problems to have affected mankind in recent decades. The waste management is become a very crucial environmental problem in the world, due to the ever increasing amount of waste material, domiciliary and industrial, generated.

The main strategies for the waste management are the protection of the environment and used to produce energy.

Lignin, the second most abundant component besides cellulose in biomass. In this study, lignosulfonate, is used as fuel in the solid oxide fuel cell to produce a power and heat, which is a byproducts from the wood pulp using sulfite pulping. To enhance the performance and conductivity of the biomass based fuel cell, the lignin was treated with hydroxides (Li/K) and chlorides (FeCl₃) at different temperature 200 - 500 °C. The maximum obtained power density was about 20 mW/cm². And the calculated electrical efficiency of the cell was about 30%.
Also, this kind of biomass fuel was used in single component fuel cell and results were compared with three components fuel cell. The phase analysis, microstructure and conductivity of lignin was analysed by XRD, SEM and AC impedance technique.

It has been concluded that a sulfonated lignin from waste of the paper industry can be used as an energy sources with fuel cell operation.

"When it seems nothing is going to work, you are usually just a few millimeters away from make it happen."

Anthony Robins

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0 Introduction

0.1 Problematic

Today, the humanity recognizes that nature is not a good unalterable, is fragile, so their conservation is a fundamental and urgent task. The Pollutants affect the air, the water, the soil and the animal and plant life.

The main reason of the air pollution is the burning of fossil fuels. As a direct problem of the burning fuels, we can find:

- The smog, a photochemical effect that produces NO\textsubscript{x}, COV's and increases the levels of ozone in the troposphere.
- The increase of levels of SO\textsubscript{2} and NO\textsubscript{x} that produces the acid rain damaging forests, water systems, agriculture and civil engineering. It's a very big problem of the Scandinavian countries and the center of Europe.
- The increases of levels of CO and CO\textsubscript{2} producing the greenhouse effect that increase the Temperature of the world causing the sea level rise and other climatic catastrophes.
- The increase of levels of heavy metal

The above mentioned pollutants are the cause of several problems that increase the vulnerability of people and make them more prone to contagious respiratory and cardiovascular disease, including the cancer development.

According to the European Commission, air pollution currently causes about 370,000 premature deaths in the European Union.

Another problem is that the population in the world is increasing and the reserves of energy resources are decreasing. As you can see in the Hubbert’s curve in the figure 0.1, right now we are in the peak oil and since now, the amount of fuel cells will decrease. This produce that an increase of the cost of the fossil fuels. In the European Union the unleaded 95 octane cost around 1,447 €.
Therefore, scientists are working on the creation of new fuels such as ethanol, methanol or hydrogen, and even new power generation systems based on chemical energy rather than combustion. The fuel cell is one of the results of this work.
0.2 Motivation

The present work consists in the study of the use of biomass for the Low Temperature Solid Oxide Fuel Cell (Forward mean as LTSOFC). I think that this study is very important for the forward reasons:

- The fuel cell has a very high efficiency.
- The study of a fuel cell is very new for me. Also the possibility of using biomass as a fuel it’s very interesting because we can reduce the amount of CO$_2$ in the atmosphere. We can resolve then the above mentioned problems.
- With the study of a LTSOFC I’ll study a new polygeneration system that produces electricity and heat which to cover the individual households need
- With the study of renewable energies I think that I can give a little bit hope to this world with the problem of pollution.

0.3 Objective

The objective of this project is to use lignosulfonated, a waste from the paper manufacturing as a fuel in to the Low-Temperature solid oxide fuel cell. With this I will use a new kind of renewable energy, the biomass, in order to do a good waste management in the paper industry.

The lignin can be used in the fuel cell directly or by pretreatment or by a steam reform process. In my project, I will use the lignin directly and by some pretreatment in order to improve the efficiency.

![Figure 0.3: Utilization of lignin in to the fuel cell](image)
1 The fuel Cells

1.1 History of fuel cells

Christian Friedrich Schönbein was the first person to discover the principle of the fuel cells in 1838. After that, in 1842 Sir William Robert Grove made the first fuel cell thanks to the work of Friedrich which produced electrical energy by combining hydrogen and oxygen. He obtained a light current and the hydrogen and oxygen were recombined producing water but at that time as shown in Figure 1.1, the high-powered steam engines were very popular and the fuel cell was forgotten. The fuel cell that he made used similar materials to today's phosphoric-acid fuel cell.

![Figure 1.1. Drawing of the first fuel cell](image)

In 1958 appeared the first commercial use of the fuel cell thanks to W. Thomas Grubb and Leonard Niedrach. They made a new type of fuel cell using a sulphonated polystyrene ion-exchange membrane as electrolyte and platinum into the membrane as a catalyst for the oxidation of hydrogen and reduction of oxygen. This cell was known as the “Grubb-Niedrach fuel cell” and it was used by the NASA and McDonnell Aircraft. [1,2]
1.2 How generally does it works?

In the figure 1.2 it’s possible to see the production of hydrogen and air thanks to the electrolysis of the water, but after that, it’s possible to change the power supply by one ammeter (like figure b) and see a little amount of current by the recombination of hydrogen and oxygen:

\[ 2H_2 + O_2 \rightarrow 2H_2O \]

![Image of electrolysis process](image)

*Figure 1.2: (a) The electrolysis of water. (b) The hydrogen and air are recombining to get some current*

Also, in the figure 1.2 is shown that the cell is constituted by the electrodes and the electrolyte. The electrolyte is strictly necessary to separate the two kinds of fuels and allow the ion exchange between the anode and the cathode. In the electrodes take place the reaction and they have to be porous to provide a good pathway. The production of electricity and power depends on the kind of fuel used and how long it’s provided. The life of the fuel cell depends on the kind of electrodes and electrolyte used.

At the anode:

\[ H_2 \rightarrow 2H^+ + 2e^- \]

At the cathode:

\[ 2H^+ + \frac{1}{2} O_2 + 2e^- \rightarrow H_2O \]

Overall reaction:

\[ 2H_2 + O_2 \rightarrow 2H_2O \]

The oxygen reacts with electrons produced at the anode whose pass through an electrical circuit to the cathode and H⁺ ions taken from the electrolyte. The mechanism can be seen in the figure 1.3. It’s very important to consider that the reactions change with the type of fuel cell and the type of fuel.
1.3 Types of fuel cell

It’s possible to classify the fuel cells according two parameters, the operating temperature and the type of electrolyte. Actually, there are six classes of fuel cell as viable systems for the present and the near future. These fuel cells are: The alkaline fuel cell, the proton exchange membrane fuel cell, the direct methanol fuel cell, the phosphoric acid fuel cell, the molten carbonate fuel cell and the solid oxide fuel cell.

The table 1.1 shows, as summarize, the different types of fuel cell.
Table 1.1: Summary of the types of fuel cell.

<table>
<thead>
<tr>
<th>Fuel Cell Types</th>
<th>Type of Electrolyte</th>
<th>Operating temperature°C</th>
<th>Electrical Efficiency</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
| PEMFC           | Polymer/solid membrane | 50-80°C                  | 53-60% (Transportation) And 25-35% (Stationary) | ♦ Low operating temperature  
♦ Absence of corrosive liquid electrolyte  
♦ Fast start-up  
♦ Simple cell structure  
♦ Potentially very low capital costs | ♦ Low CO tolerance  
♦ Drying of membrane  
♦ Waste heat has low value  
♦ Low performance of the cathode |
| AFC             | Aqueous alkaline     | 50-200°C                  | 60%                   | ♦ Mature technology  
♦ Reliable  
♦ High efficiency  
♦ Low cost materials | ♦ PEFC is superior in many applications  
♦ Not CO2 tolerant |
| PAFC            | Phosphoric acid      | 200-250°C                 | 40%                   | ♦ Mature technology  
♦ Very reliable  
♦ Fast response time  
♦ High efficiency with partial loads | ♦ Too expensive  
♦ Rather low efficiency  
♦ Waste heat has low value  
♦ CO < 1% |
| MCFC            | Molten carbonate     | 600-700°C                 | 45-47%                | ♦ High efficiency  
♦ CO tolerant  
♦ Internal reforming Possible  
♦ No noble metal catalysts  
♦ High-quality waste heat | ♦ Material problems of cell and stack components  
♦ Need of CO2 circulation  
♦ Sulphur tolerance is low (<1 ppm) |
| SOFC            | Solid Oxide          | 600-1000°C                | 35-45%                | ♦ Very high efficiency  
♦ High-quality waste heat  
♦ Simple system  
♦ No reformer needed (at least not for CH4)  
♦ Fuel flexibility  
♦ Sulphur tolerance is at least one order of magnitude higher than for MCFC | ♦ Still far too expensive, because of the synthesized ceramic materials  
♦ Thermal expansion  
♦ Porosity  
♦ Temperature gradients  
♦ Mixed conduction problems |

As is possible to see on this table the Solid Oxide fuel cell (SOFC) has a very good advantage in comparison of the others fuel cells, the fuel flexibility. That’s why the SOFC is used in this project.

1.4 Fuels for fuel cells

The most common fuels used in the fuel cells are the hydrogen and some hydrocarbons like coal gas, natural gas….But also, it’s possible to find some liquid fuels like ethanol, methanol, liquefied petroleum gas…. or even solid like the lignin, a waste from the paper manufacturing.

Normally, it is better to use hydrogen as fuel because it is good for the environment, but, sometimes other fuels are used for some problems like the storage of hydrogen.

Hydrogen is the favourite fuel for the fuel cells because the only product that it gives is water, which is environmentally benign. The hydrogen use to be a gas very flammable, it can burn in air at a very big range of concentration (5-75%):

\[ 2H_2 + O_2 \rightarrow 2H_2O \]
There are many ways to produce Hydrogen. One of the ways to make Hydrogen is the electrolysis of water. For this is necessary to give electrical power to two electrodes placed in the water:

\[
2 \text{H}_2\text{O}(l) \rightarrow \text{O}_2(g) + 4 \text{H}^+(\text{aq}) + 4 \text{e}^-
\]

\[
2 \text{H}_2\text{O}(l) + 2 \text{e}^- \rightarrow \text{H}_2(g) + 2 \text{OH}^-(\text{aq})
\]

In the cathode takes place the formation of hydrogen and in the anode the formation of oxygen. So the overall reaction is: \(\text{H}_2\text{O}(l) \rightarrow \text{H}_2(g) + \text{O}_2(g)\)

Assuming ideal faraday efficiency, the amount of hydrogen generated is twice the number of moles of oxygen, and both are proportional to the total electrical charge conducted by the solution. The electrolysis of pure water requires a lot of energy due to the self-ionization of water, that's why it's very normal to add one electrolyte (such as a salt, an acid or a base) to increase the efficiency.

It’s a very good idea to produce the electrical power by renewable energy (solar, wind, wave…)

The most economically way is using processes to remove the hydrogen from hydrocarbons like petroleum, coal, coal gases, natural gas… One of the processes can be the steam reforming of natural gas at high temperatures:

\[
\text{C}_n\text{H}_m + \text{H}_2\text{O} \rightarrow n\text{CO} + (m/2 + n)\text{H}_2
\]

For the production of high purity hydrogen is normal to use the water-gas shift reaction in conjunction with the steam reforming:

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2
\]

These two reactions are carried out normally over a supported nickel catalyst at elevated temperatures, typically above 500 °C. Also is very important to know something about the physical and combustion characteristics of the fuel and also his chemical composition. The chemical composition will determine the
type of fuel processing to produce hydrogen.
A similar method to produce hydrogen is the pyrolysis of the hydrocarbon. The pyrolysis consists on heat the hydrocarbon fuels in the absence of air to decompose it into hydrogen and solid carbon.

But, before fed the cell with one of these fuels, is very important to do some process for the conversion of the raw primary fuel into the fuel gas required by the stack. Each type of fuel cell stack has some particular fuel requirements as you can see in the next table:

Table 1.2: The fuel requirements for the different types of fuel cells

<table>
<thead>
<tr>
<th>Gas species</th>
<th>PEM fuel cell</th>
<th>AFC</th>
<th>PAFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>Fuel</td>
<td>Fuel</td>
<td>Fuel</td>
<td>Fuel</td>
<td>Fuel</td>
</tr>
<tr>
<td>CO</td>
<td>Poison</td>
<td>Poison</td>
<td>(&gt;0.5%)</td>
<td>(&lt;1.0%)</td>
<td>(&lt;0.5%)</td>
</tr>
<tr>
<td>CH₄</td>
<td>Diluent</td>
<td>Diluent</td>
<td>Diluent</td>
<td>Diluent</td>
<td>Diluent</td>
</tr>
<tr>
<td>CO₂ and H₂O</td>
<td>Diluent</td>
<td>Poison</td>
<td>Unknown</td>
<td>Poison</td>
<td>Poison</td>
</tr>
<tr>
<td>S (as H₂S and COS)</td>
<td>Few studies, to date</td>
<td>Poison</td>
<td>Poison</td>
<td>Poison</td>
<td>Poison</td>
</tr>
</tbody>
</table>

*In reality CO reacts with H₂O producing H₂ and CO₂ via the shift reaction 8.3 and CH₄ with H₂O reforms to H₂ and CO faster than reacting as a fuel at the electrode.

*A fuel in the internal reforming MCFC and SOFC.

*The fact that CO₂ is a poison for the alkaline fuel cell more or less rules out its use with reformed fuels.

For example, is very important to take out the sulphur with a hydrodesulphurisation reactor because it deactivates the steam reforming catalysts or poisons the cell. [1]

Of course, is better for the environment to use renewable fuels for these processes like biofuels or wastes instead fossil fuels. It’s possible to obtain energy from the biomass by different ways like:

- Direct combustion
- Conversion to biogas via anaerobic digestion
- Conversion to ethanol via fermentation
- Conversion to syngas

Also it is possible to get bio-fuels from the wastes. The combustible components of such waste may be extracted chemically by conversion to gases, liquid distillates or biochemically by anaerobic digestion using methane-forming bacteria. Of course, the biogas has high values of carbon monoxide making it unattractive for use in gas engines, but, it can be used on MCFC or SOFC cells which are able to handle very high levels of carbon oxides. Bioliquids like methanol and ethanol are also attractive for the fuel cells, we can produce methanol from syngas made by biomass and ethanol by the fermentation of biomass.
The next picture shows the different ways for supply hydrogen in the fuel cells:

![Diagram of hydrogen supply methods]

*Figure 1.5: How to supply Hydrogen in a fuel cell*

In this work I will discuss about the SOFC. The SOFC has a superior approach that it can be use more than one fuel. Particularly it is used for the hydrogen gas but later it shows that it can be used for the liquid and solid also. It's a good idea also to feed this cell with bio-ethanol or bio-methanol.

In North America, they get the ethanol from the corn and in Brazil from the sugar cane. If ethanol is directly exposed to the environment by, for example, by one leakage, it is not harmful. The ethanol made from the corn gives a 35% of energy and the ethanol made from the sugar cane gives 700%, but the conditions for the cultivation are more stringent. Also is more easy to transport and store than the hydrogen. That's why the ethanol is a good alternative of fuel. [5,7]

The methanol is toxic and poison but not considers a carcinogenic and harmful for the environment.

At anode: \[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 6\text{H}^+ + 6e^- \]
At cathode: $$3/2 \text{O}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow 3\text{H}_2\text{O}$$

Overall Reaction: $$\text{CH}_3\text{OH} + 3/2 \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3\text{H}_2\text{O}$$

It's possible too to feed the fuel cell with carbon directly. Direct carbon fuel cell (DCFC), using molten hydroxide as electrolyte, achieves 0.75 and 0.85 V of OCV with a peak power output of 180 mW/cm² and a maximum current density of 250 mA/cm² at 600 °C. [28]

### 1.5 The Applications of fuel cells

The potential applications of fuel cells are increasing due to the different benefits that it gives. The two most important are the environmental considerations (no NOx, SOx, or hydrocarbon emissions and no or much reduced CO₂ emissions) and the efficiency considerations (The efficiency is better for a fuel cell than for a thermal machine).

The fuel cells can be used in a wide range of applications due to the different types that exists and they can also work from a few watts to megawatts. The fuel cells can be used in three different fields: Combined heat and power systems and mobile power systems.

**Mobile application**

The fuel cells give higher power densities than batteries, that's why is very important to use the fuel cell in some devices where only few watts are required like palm-top, lap-top computers, mobile phones and other portable electronic devices.

Also, thanks to reduced emissions of pollutants and for the high efficiency, it's possible to use the fuel cells on vehicles. This idea is very important for the urban areas where localised pollution is a major issue. The good fuel cells for this transport application are the fuel cells which work at low temperature because of the need for short warm-up and cool-down times (PEM fuel cell). The problem is that is very expensive to fuel with hydrogen, but, In the case of public transport in cities, hydrogen is a realistic fuel since buses can be refuelled with hydrogen at a central depot. There are some busses running with hydrogen in some cities; the compressed hydrogen is stored in tanks in the roof, which can give a range of up to 300 km and a top speed of 80 km/h. However, some companies are working for the fuel cell car. Different companies like Toyota or Ford selected methanol as fuel for the car but other companies chose the hydrogen like Daimler-Benz, which build a first car in 1994 fuelled by hydrogen.
Combined heat and power applications (CHP)

Here the fuel cells operate from more or less than 1 kW to several MW which covers individual households and industries providing all the power and hot water from a single system. They offer greater efficiency than the current situation where electricity is distributed from a small number of centralised power stations and the heat is supplied by boiler units in each house. Normally the fuel cells used are which work at high temperature where the heat produced is used to drive a gas turbine to produce more electricity. It’s possible to use the fuel cells for small-scale, stand-alone and remote applications like gas pipelines, farms, caravans… [1], [8]

![Figure 1.6: Some applications of the fuel cells](image)

1.6 Theory of the fuel cells

1.6.1 Thermodynamically basis

To understand the theory of fuel cells, I think it is necessary to review the knowledge of the thermodynamic. First I will discuss the first law of thermodynamics, which is also known as the law of energy conservation, after this, I will see the second law and the exergy term.

First principle

The first explicit statement of the first law of thermodynamics was given by Rudolf Clausius in 1850:

*"There is a state function E, called ‘energy’, whose differential equals the work exchanged with the surroundings during an adiabatic process."*
The first law says that the total variation of the energy (kinetic, potential or internal) of one system is equal to the difference between the transferred heat to the system and the work that the system gives. The mathematical equation is:

\[ dE = dQ + dW \]  

1.1

So, this law says that is impossible to produce work by a cyclic machine without consume the same quantity on energy.

I can see the energy as three forms, the kinetic energy \( K \), the potential energy \( V \), and the internal energy \( U \). This last one is due to molecular motions and intermolecular interactions.

\[ E = K + V + U \]

Normally, in our experiments I consider \( K \) and \( V \) equal to 0, then:

\[ dU = dQ + dW \]  

1.2

\( Q \) is a kind of energy whose can be transferred by conduction, convection or radiation. When I work at constant pressure, like our case, I can consider the heat like the enthalpy \( H \), a state function.

\[ H = U + PV \]  

1.3

At constant pressure it's possible to write this:

\[ dH = dQ = C_p dT \]  

1.4

\( C_p \) is the heat capacity, is the measurable physical quantity that characterizes the amount of heat required to change a substance's temperature by a given amount.

For a reaction like \( aA + bB \rightarrow cC + dD \) I can write the enthalpy reaction as:

\[ \Delta H = c\Delta H_{fC} + d\Delta H_{fD} - a\Delta H_{fA} - b\Delta H_{fB} \]  

1.5

In this equation, \( \Delta H_{f} \) is the formation enthalpy of the compound at one Temperature. Normally, this kind of enthalpy is tabulated for 25 °C as a reference temperature and is the enthalpy reaction for the formation of one mole of the pure substance at this Temperature.

Also, for a constant pressure, the enthalpy reaction is equal to the heat which gives the reaction. If the reaction is exothermic then \( \Delta H<0 \) and for an endothermic reaction \( \Delta H>0 \). [9]

The work \( W \) is very similar to the heat, is not a state function is a way to transfer energy. There are many types of work like, for example, the expansion-compression work:

\[ dW = pdV \]  

1.6
Another kind of work is the electrical work:

\[ dW = -Edq \]

It's possible to obtain some work when a potential difference causes an electrical charge flow. If I divide by the time I obtain the power.

\[ dw = -E \frac{dq}{dt} = -Ei \]

\( i \) is the current.

**Second principle**

The first theory of the conversion of heat into mechanical work is due to Nicolas Léonard Sadi Carnot in 1824. He was the first to realize correctly that the efficiency of this conversion depends on the difference of temperature between an engine and its environment. But, the Carnot work doesn't had much influence at that moment, but after, in 1850, Rudolph Clausius corrected this work with the help of the first law of thermodynamic and he was the first to formulate the second law of thermodynamic in this form:

"Heat does not flow spontaneously from cold to hot bodies".

After, Kelvin-Planck formulates the second law by this way:

"Is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work"

With the second law, we can deduce the performance of a Carnot engine, according to the Carnot’s principle:

"No engine can be more efficient than a reversible engine operating between the same high temperature and low temperature reservoirs. All irreversible heat engines between two heat reservoirs are less efficient than a reversible Carnot engine operating between the same reservoirs"

For deduce the rule it’s important to see the figure 1.14:
In this figure, the engine receives heat from the high temperature reservoir and it gives work and a quantity of heat to a low-temperature reservoir obeying the second law. The efficiency of this engine is:

\[ \eta_{\text{Carnot}} = \frac{W_{\text{net}}}{Q_h} \quad 1.8 \]

According to the first principle, the energy conserves:

\[ 0 = Q_h - Q_l - W_{\text{net}} \]

\[ \eta_{\text{Carnot}} = \frac{W_{\text{net}}}{Q_h} = \frac{Q_h - Q_l}{Q_h} = 1 - \frac{Q_l}{Q_h} = 1 - \frac{T_l}{T_h} = \frac{T_h - T_l}{T_h} \quad 1.9 \]

**Exergy**

As engineer I have to focus on the exergy, the maximum useful work. For example, if we burn a quantity of combustible, we can get a hot mix of air and combustion products and the energy of the system is conserved, but, the capacity to produce useful work is now lower than before. So, it's very interesting to get a property which quantifies the maximum useful work.

This property is the exergy. The maximum useful work that the system can give us will depend on the initial state, final state and the type of process. It's a state function.

The work will be maximum if the process is reversible and if the system is in thermodynamic equilibrium.
with the environment at the end of the process. At the end of the process, the system will have energy but it can’t give work, the exergy is 0.

There are always some differences between the real work that the system gives us and the exergy. For the engineers, the objective is to minimize these differences. The exergy is destroyed by the irreversibilities and it depends on the system and environment state. [10]

1.6.2 Thermodynamic in fuel cells

In the Carnot engines the thermal energy source comes from the spontaneous reaction between the fuel and the oxidant. With this, we obtain the thermal energy which can be transforms in work.

But, there is a better way to transform the chemical energy into work deleting the irreversible steps due to a non-controlled exchange process of electrons between the reactants. It’s possible to control this process if we change the system of combustion by a fuel cell. So, the fuel cell can be represented as a device where the fuel and the oxidant participate in a chemical reaction controlled giving the products of the reaction and current directly.

It’s very important to know the chemical energy produced by the fuel cell. In the case of fuel cell the chemical energy is the Gibbs free energy which can be defined as the energy available to do external work, neglecting any work done by changes in pressure or volume. This external work is the movement of the electrons round an external circuit and the exergy in this case, is all the external work that can be extracted, including that due to volume and pressure changes.

So, the external work is the electrical work that we saw before in 1.7. It’s possible to demonstrate this if we consider that the work is the movement of the electrons round an external circuit. For example, if we use Hydrogen as a fuel, for each molecule of water produced I have 2 electrons which pass round the external circuit. So, for a mole of hydrogen 2N moles of electrons pass round the circuit and N is the Avogadro’s number. If e is the charge of one electron, the charge that flows is:

\[-2Ne = -2F\]

E is the voltage of the fuel cell, so, the electrical work is

\[dW = -Edq = -nFE\]

n is the number of electrons produced for each molecule of fuel used. Also:

\[\Delta G = dW = -nFE\]

1.10

For a general gas reaction with A and B as a reactants and C and D as products:
A + B □ C + D

The Gibbs free energy can be expressed like this with the standard Gibbs free energy:

$$\Delta G = \Delta G^\circ + RT \ln \frac{P_C^d P_D^d}{P_A^a P_E^b}$$

1.11

Where $P$ is the partial pressure of the reactants and products of the reaction and $\Delta G^\circ$ is the gibbs standard energy of the reaction. Now, it's possible to calculate the ideal standard potential, $E$.

$$-nFE = -nFE^\circ + RT \ln \frac{P_C^d P_D^d}{P_A^a P_E^b}$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{P_C^d P_D^d}{P_A^a P_E^b}$$

1.12

This equation is also called the Nernst equation.

Usually, the fuel cell has to burn the fuel to release their energy, so, it's normal to express the efficiency of the fuel cell like the comparison between the electrical energy produced and the heat that would be produced by burning the fuel. The reaction enthalpy $\Delta H$ is the heat delivered by the chemical reaction, so, the efficiency is:

$$\varepsilon = \frac{W_{\text{elec}}}{\Delta H} = \frac{\Delta G}{\Delta H} = -\frac{nFE}{\Delta H}$$

1.13

This equation represents the maximum efficiency limit of the fuel cell.

If the cell operates at low temperature, the voltage losses will increase, so, in practice, the fuel cells have higher performance at high temperature. Also, at high temperature It's possible to use the waste heat of the fuel cell.

Therefore the efficiency of a fuel cell should be compared to the theoretical efficiency of a heat engine as e.g. the internal combustion engine of our cars.
Figure 1.8: Comparison of the efficiency of the fuel cell with other engines.

The fuel cells have a better performance than the Carnot engines (Figure 1.8). However, the fuel cells have some losses too. [1] [4]

1.6.3 The losses of the Fuel cell

It’s possible to know the voltage for a fuel cell working at 100 °C with Hydrogen as a fuel:

\[ E = \frac{\Delta G_f}{nF} \]  

\( \Delta G_f \) is the Gibbs free energy of formation and his value is tabulated for each compound at different Temperature.

For this fuel cell, the voltage is 1.2 V, however, when the cell works the voltage is less than 1.2 V. If I put in a graph the Cell voltage in V versus the current density in mA/cm², it’s possible to see that even the OCV is less than the theoretical value; there is a rapid fall in voltage. After this, when the current density increases, the voltage decreases less rapidly and more linearly than before. Nevertheless, it’s possible to decrease the difference between the theoretical value and the actual operating voltage increasing the Temperature.

The comparison is shown in the next figure.
Figure 1.9: The first graph shows the voltage and current density for a low-temperature fuel cell, and the second for a fuel working at 800 °C.
Also, the initial fall in voltage is very small and the graph is more linear. That’s because at high temperature the voltage drop is smaller.

This is due to four major irreversibilities:

- **Activation losses:** The reaction takes a long time to take place on the surface of the electrodes. That’s because a proportion of the voltage generated is lost in driving the chemical reaction that transfers the electrons to the electrode.
- **Fuel crossover and internal currents:** This energy loss takes place because sometimes the waste of fuel and/or, to a lesser extent, the electrons can pass through the electrolyte.
- **Ohmic losses:** These losses are related with resistance to the flow of electrons through the electrodes and other interconnections and the resistance to the flow of ions through the electrolyte. This lose is proportional to current density.
- **Mass transport or concentration losses:** The concentration of the reactants affects voltage, so, these losses come from the change in concentration of the reactants at the surface of the electrodes as the fuel is used. This type of loss has a third name – ‘Nernstian’. This is because of its connections with concentration, and the effects of concentration are modelled by the Nernst equation.

### 1.6.4 The Total efficiency of a fuel cell

Since now, I just talked about the electrical efficiency, but also, and especially for fuel cells which work at high temperature, it’s important to consider the heat efficiency. So the total efficiency of a fuel cell is the electrical efficiency plus the heat efficiency. The total efficiency can be show also as this equation:

$$\eta_{Total} = \frac{Q_{used} + \text{power}}{Q_{provided, to, system} + \text{Energy, content, of, fuel}}$$  \hspace{1cm} 1.15

$Q_{used}$ is the heat that I can benefit from the output gases of the fuel cell. The system works at constant pressure so, the heat it's equal to the enthalpy variation. [1],[4]
2 The Solid oxide fuel cell

In this work I will use the solid oxide fuel cell to make my experiments, so, in this chapter I will talk about the actuality of the SOFC.

2.1 Principle of a solid oxide fuel cell

The mechanism of this fuel cell is different to the generally mechanism. The oxygen is reduced to oxygen ions which pass through the solid electrolyte to the anode where they reacts with the hydrogen or the other fuels like carbon monoxide giving, water in the case of the hydrogen, and carbon dioxide in the case of the carbon monoxide as well as electricity and heat.

![Mechanism of the solid oxide fuel cell](image)

*Figure 2.1 Mechanism of the solid oxide fuel cell*

With this kind of fuel cells, it's normal to achieve a performance of 80%. The SOFC operates at elevated temperatures, conventionally between 800-1000 °C, though there is considerable interest in lowering the operating temperature of smaller SOFCs in particular to reduce costs. The good advantage that the high temperature gives, it's that is possible to feed directly the cell with hydrocarbon fuels without the need of a complex and expensive external fuel reformer. [8] [4]
2.2 Constitution

Like the other fuel cells, the SOFC is constituted by an anode, a cathode and a solid oxide electrolyte. The different components of the fuel cell should have good chemical and physical stability in their environment, should be chemically compatible with the other components, and should have good conductivity and similar thermal expansion coefficient to avoid problems like the delamination or cracking during the fabrication or the operation.

2.2.1 Electrolyte

The function of the electrolyte is to separate the two gas atmospheres and to transport the oxygen-ions from the cathode to the anode. It should be fully dense to stop short-circuiting of reacting gases and It has to be resistant to the oxidizing conditions. The transport of the oxygen-ions is due to the vacancies in the oxygen sub lattice.

Also, the electrolyte has to be as thin as possible to minimize the voltage losses. The thickness of the electrolyte depends on the cell design and in the mechanical stability of the electrolyte.

In the actuality, the electrolyte used is yttria-stabilised zirconia which has good oxygen ion conductivity, good stability in reducing and oxidizing atmospheres, a relatively low cost and is abundant and easy to fabricate.

2.2.2 Anode

Here, the fuel will be oxidized in the presence of oxygen. It's very important that the anode must not be oxidized under the operating conditions. The majority of fuel cells have Ni as metal for the anode because it can work at high temperature and has a low cost if I compare with other metals which can work at high temperature like Co or noble metals. Also, the metal must have a porous structure which can resist the higher temperatures.

This property, can be obtained if the electrode is mixed with electrolyte forming a cermet composite which maintains the porosity, prevent the sintering of the nickel and gives a thermal expansion coefficient very similar to the electrolyte.

2.2.3 Cathode
Like the anode, the cathode has to be very conductor and also it must have a porous structure but it has to be stable in an oxidizing atmosphere.

As I said before, the SOFC works at very high Temperature so, this temperature restricts the material selection to the noble metals or electronically conducting oxides, but, the noble materials are excluded for their high prices. Of course, the cathode must have the same thermal expansion coefficient than the electrolyte and it doesn’t have to react with the electrolyte. The most used material for the cathode is the Strontium-doped lanthanum manganite (LSM) a perovskite material with intrinsic p-type conductivity. The cathode is produced with a lanthanum deficiency to avoid the disintegration with the formation of La₂O₃.

The cathode is made by two layers. Normally, one layer is the mixture between the LSM with the yttria-stabilised zirconia to make a cermet like with the anode. This method, improves the thermal match of the cathode with the electrolyte, the porosity and the resistance to sintering. The second layer is only pure LSM and is called current collect layer. It’s possible to improve cell performance if I add at the cathode some quantity of platinum.

The table below shows the different materials used in the actually of SOFC.

<table>
<thead>
<tr>
<th>Component</th>
<th>ca. 1965</th>
<th>ca. 1975</th>
<th>Current Status</th>
</tr>
</thead>
</table>
| Anode     | Porous pt. | Ni/ZrO₂ cermet | ✓ Ni/ZrO₂ cermet  
                        ✓ Deposit slurry, EVD fixed  
                        ✓ 12.5 × 10⁻⁶ cm/cm °C  
                        ✓ □ 150 µm thickness  
                        ✓ 20-40% porosity |
| Cathode   | Porous pt. | La₁₋ₓSrₓMnO₃ mixed with electrolyte | ✓ Doped Lanthanum manganite  
                        ✓ Extrusion, sintering  
                        ✓ □ 2 mm thickness  
                        ✓ 11 × 10⁻⁶ cm/cm °C expansion from room temperature to 1000°C  
                        ✓ 30-40% porosity |
| Electrolyte | Yttria stabilized ZrO₂  
             0.5-mm thickness | Yttria stabilized ZrO₂ | ✓ Yttria stabilized ZrO₂ (8mol% Y₂O₃)  
                                      ✓ EVD  
                                      ✓ 10.5 × 10⁻⁶ cm/cm °C expansion from room temperature to 1000°C |
### 2.3 Designs of solid oxide fuel cell

There are two types of design, the tubular and the flat plate shapes.

**Tubular shape**

It was developed by Siemens-Westinghouse and it’s the best design for the SOFC. The thickness of the cathode, electrolyte and anode layer are around 2 mm, 40 and 100 µm respectively. Cells with a length of 150 cm normally have 1036 cm² of active area! The cells are connected in series by using ceramic LaCrO₃ interconnection, and in parallel by using Ni-felts. The cells and bundles have been demonstrated for more than 25 000 h of operation, the power density achieved is around 0.2 W/cm² and the fuel utilization is almost 90 % at 1000 ºC.

The major disadvantage in the cell design that limits the performance is the ohmic loss due to the long current pathways in the thin and porous layers.

The cell is supported by the cathode mainly.[4]

**Flat plate shape**

The cell consisting of anode, electrolyte and cathode layer is sandwiched between the interconnection plates. The current flow is perpendicular to the cell surface resulting in short current pathways in a stack.

The interconnection has two functions, one is to be the electrical contact between the elements and the other one is to supply fuel gas and air to the anode and the cathode. Here, the cell can be supported by the cathode or by the electrolyte.

In the figure below, you can see the two types of design.
2.4 Comparison of SOFC with other fuel cells

One of the most different parameter between the SOFC and the other fuel cells is the Temperature. Normally, the SOFC works at 800-1000 °C and this allows the internal reforming inside the cell, at the anode, also it’s possible to use the cell for warm the water and the efficiency increases a lot. It’s possible to see in the figure 2.4 the comparison of the efficiency of SOFC with the efficiency of other cells. Also the durability of the SOFC is higher than the other cells and is very friendly with the environment. It has a good fuel flexibility that allows the use of biomass as a fuel. The comparison of the different cells emissions for the same fuel is shown in the table 3.2

Table 2.2: Comparison of different cells emissions

<table>
<thead>
<tr>
<th></th>
<th>PEM</th>
<th>PAFC</th>
<th>SOFC</th>
<th>MCFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx (lb/MWh)</td>
<td>0.06</td>
<td>0.03</td>
<td>0.01</td>
<td>0.05</td>
</tr>
<tr>
<td>SO2 (lb/MWh)</td>
<td>TBD</td>
<td>0.006</td>
<td>0.005</td>
<td>TBD</td>
</tr>
<tr>
<td>PM-10 (lb/MWh)</td>
<td>TBD</td>
<td>0</td>
<td>0</td>
<td>TBD</td>
</tr>
<tr>
<td>CO2 (lb/MWh)</td>
<td>1.360</td>
<td>1.078</td>
<td>950</td>
<td>~900</td>
</tr>
</tbody>
</table>
2.5 Applications of SOFC

One of the most important applications is the polygeneration. The term ‘polygeneration’ is most widely used to describe the generalisation of the idea of ‘cogeneration’ (i.e. the thermodynamically efficient use of fuel) in the form of systems which simultaneously produce more than one form of energy to the final user, for example: electricity, heating and cooling.

According to [2004/8/EC], “cogeneration” shall mean the simultaneous generation in one process of thermal energy and electrical and / or mechanical energy”. On the basis of this definition, ‘polygeneration’ would be the simultaneous generation in one process of more than two energy carriers. The European Commission published in 2004 the directive on promotion of cogeneration [2004/8/EC], with the purpose to “facilitate the installation and operation of electrical cogeneration plants in order to save energy and combat climate change.”

The main benefit of polygeneration is to save primary energy sources, e.g. to actively use the ‘waste’ heat of the power generation process. Figure 2.5 illustrates this fact considering the simple example of...
cogeneration and showing how much primary energy would be used in single plants to deliver the same amount of electrical and thermal energy of an equivalent cogeneration plant.

Communities are thus choosing polygeneration for two main reasons:

- Optimisation of the use of primary energy sources: one unit of primary energy source can be used to provide more useful energy than a single plant without polygeneration. In this way, the energy losses of the single processes are reduced and the energy balance of the community is greatly improved. In other words, there is no reason to get rid of the heat generated in a thermoelectric process if biomass has to be burned again to cover the heating needs.

- Polygeneration can be used to convert local available energy or material resources into other forms of energy or materials, which ideally should also be used at local level. Primary energy sources, high temperature heating energy or by-product of other processes can be used. The community should thus first check if any resources are already available at community level in order to cover community energy needs, before importing additional primary energy sources.
The high flexibility of solid oxide fuel cells (SOFC) on fuels allows it for typically use with a large spam of fuels and make it easy for the future. SOFC coupled with highly efficient energy transformation, this characteristic could become an important basis for plants allot to the reduction of greenhouse gas emissions, and for the widespread use of residential renewable fuels.

Siemenes-Westinghouse installed a test plant of 100 kW in Netherlands which operated for more than 16 000 hours in total. The hot off-gas from the stack is used to preheat the air and produce steam prior to being supplied to the local district heating system. The system has an electrical efficiency of 43%.

The particular advantage of stationary SOFC systems is that the hot SOFC off-gas can be used in a gas or steam turbine in a combined cycle.

Recently, SOFC systems for domestic/Small business application have been attracting considerable interest. The first system currently in the field test phase is the Hexis system developed by Sulzer for a CHP with a power output of 1 kW. The electrical efficiency is 35%. [11], [12], [13]

Also, since 1998, SOFC systems for mobile applications have been under development. Targeted applications in the automotive area are auxiliary power units for passenger cars or trucks.
2.6 Solid oxide fuel cells + gas turbine

The solid oxide fuel cell appears better suited to power generation in a hydrocarbon fuel economy. Moreover, due to the synergistic effects, hybrid SOFC and gas turbine technology has been identified to be a superior power-generation technology to many other options. For a small-scale, electrical power-generation systems consisting of advanced microturbines and SOFC stacks, with a power rating of 250 kW, an electrical efficiency of 65% can be expected.

Some author did the model of a system with a hybrid SOFC-GT shown in the next figure:

![Diagram](image)

**Figure 2.6: The system of IRSOFC-GT**

The system consist in an internal-reforming SOFC stack, a combustor, a GT and a power turbine, two compressors and tree recuperators. The mechanical work done by the GT is used to run the two compressors and the sole mechanical power available for electrical power generation derived from the power turbine. The fuel is preheated thanks to the recuperators 1 and 2 prior to entering in to the IRSOFC stack and the recuperator 3 warms water. [14]

This system was modelling by the software tool MATLAB and the results are shown in the table 3.3
2.7 Low-Temperature solid oxide fuel cell

In the present solid oxide fuel cell (SOFC) R&D, many efforts are contributed to reduce the operation temperature either by using thin film technology for yttrium stabilized zirconia (YSZ) electrolyte or by using alternative electrolyte materials, such as various ionic doped ceria and lanthanum gallate electrolytes, etc. That can make the SOFCs function at lower temperatures.

All these efforts have, however, limitations due to the deficiency of technology and the instability of the material.

Low temperature operation (300-600 °C) for SOFCs is realized based on a research breakthrough in innovative nano- and hybrid conducting ceria-based composite materials. These materials were prepared usually by mixing different cationic doped ceria, e.g. gadolinium doped ceria (GDC), yttrium doped ceria (YDC) and samaria doped ceria (SDC) with various salts, e.g. chlorides, fluorides, hydroxides and carbonates, or by two rare-earth oxides based on the ceria. The materials contain at least two phases, e.g. the ceria phase and the salt phase, or the ceria phase and other rare-earth oxide phase different from ceria.

High ionic conductivity, varying from 0.01 to 1 S cm$^{-1}$ between 300 and 700 °C, has been achieved for the hybrid and nano-ceria composite electrolyte materials, demonstrating a successful application for advanced low temperature solid oxide fuel cells (LTSOFCs). The performance of 0.15–0.25 W cm$^{-2}$ was obtained in temperature region of 320- 400 °C for the ceria-carbonate composite electrolyte, and of 0.35-0.66 W cm$^{-2}$ in temperature region of 500-600 °C for the ceria-lanthanum oxide composites. The cell could even function at as low as 200 °C. The cell has also undergone a life test for several months.
The excellent LT SOFC performance is resulted from both functional electrolyte and electrode materials. The electrolytes are two phase composite materials based on the oxygen ion and proton conducting phases, or two rare-earth oxides. The electrodes used were based on the same composite material system having excellent compatibility with the electrolyte. They are highly catalytic and conductive thus creating the excellent performances at low temperatures. These innovative LT materials and LT SOFC technologies would open the door for wide applications, not only for stationary but also for mobile power sources. [15]

In Kungliga Tekniska Högskolan, Dr. Bin Zhu and his team, use NSDC as electrolyte for the LT SOFC. The material consist of two phases, one host face of SDC (Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$) and a second amorphous salt phase of Na$_2$CO$_3$. The nanocomposite electrolyte shows super ionic conductivity above 300°C, where the conductivity reaches over 0.1 S cm$^{-1}$. Compared with the single phase electrolyte (SDC, YSZ...), composite electrolyte contains lots of interface regions between the two constituent phases. The interface supplies high conductivity pathway for ionic conduction, which have the capacity to increase mobile ion concentration than that of the bulk. On the other hand, amorphous Na$_2$CO$_3$ plays an important role in superionic conductivity of the electrolyte. [26]

It's possible to obtain a lot of advantages with the LT SOFC:

- It increases the conductivity of the material even at low temperature.
- The size of the particles also reduces at nano levels.
- It gives more homogenous and smooth composite structure.
- It also improves the ceria-carbonate conductivity.
- Martial handling and making cell is better than the one phase.

2.8 Single Component

Currently, the fuel cells are very expensive to produce. The conventional fuel cell consist in three components, the cathode, the electrolyte and the anode, but now, Dr. Bin Zhu have achieved a breakthrough in fuel cell technology by developing a electrolyte-free-single-layer fuel cell (Single component). The device consists of a homogeneous composite layer of an ionic conductor and a metal oxide which works as a biocatalyst.

Dr. Zhu, compared two devices. One was a three component fuel cell with LiNiO$_2$-GDC as anode and GDC as electrolyte and the other one was only a layer of LiNiO$_2$-GDC (Single component). At 550 C, the three component fuel cell achieved a maximum power density of 408 mW/cm$^2$ and the single component 450 mW/cm$^2$ with hydrogen as a fuel. It is surprising that the single component device displays no short
circuit at all and achieves even higher OCV and better performance. The single component device can perform the same function as fuel cell and convert the chemical energy of H₂ to electricity continuously.

\[ 2H_2 \rightarrow 4H^+ + 4e^- \]
\[ 2O_2 + 4e^- \rightarrow 2O_2^- \]
\[ 2H_2 + O_2 \rightarrow 2H_2O \]

During this process, the H₂ contacting side acts as a “functional” anode to release electrons by forming H\(^+\), and the air O₂ contacting side as a “functional” cathode to receive electrons. All reactions and processes are completed on the surfaces of the particles in the material through direct combination between H\(^+\) and O\(^2-\) ions without involving the electrolyte process. At this stage, detailed mechanisms for the single component device are not yet clear. More works have to be done to investigate the detailed mechanism of the single component fuel cell.

---

**Figure 2.7:** Comparison between conventional three component fuel cell with the single component.
3 Biomass

3.1 The Biomass and Bioenergy

The biomass is one kind of renewable energy source used for generate electricity or produce heat. It's the organic compounds produced from the activities of living creatures which can be used as energy or material feedstock like the wood, organic waste…

Normally the way to use biomass is burning the biological material, but, it can be used too for the production of fibers or chemicals (bioproducts). It's possible to use forest residues (as dead trees, branches, tree stumps…), agricultural wastes (Animal slurry, Grass stilage, Straw…) or biodegradable wastes (as food waste, garbage, landfill gases, industrial waste …) as biomass.

![Different sources of biomass](image)
The most important physical qualities for the biomass are humidity, which has the greatest effect on heating value, particle size (which influences the treatment of the biofuel), and density. The most important chemical qualities are the heating values, especially the net calorific heating value as received. On a dry-weight basis, heating values range from about 17.5 GJ/t (herbaceous masses) to about 20 GJ/t (woody masses), this is low compared to coal (30-35GJ/t) [23]. Heating value is defined as the amount of energy released when a fuel is burned completely in a steady-flow process and the products are returned to the state of the reactants.

With the last years, and due to the problems of pollution and the energy cost, the consumption of biomass has increase.

![Figure 3.2: Consumption of biomass in the world](image)

The biomass can be converted by different ways in to bioenergy giving biofuels or producing heat and electricity. This kind of energy can help us to reduce the amount of CO$_2$ in the atmosphere. Of course, during the production of energy through the biomass there is a production of CO$_2$ because we burn it, but, this CO$_2$ can be used after by the source of biomass (Wood, crops…).

A major part of this biomass use is non-commercial and relates to charcoal, wood and manure used for cooking and space heating, generally by the poorer part of the population in developing countries. Modern bioenergy use (for industry, power generation, or transport fuels) is making already a significant contribution, and this share is growing. The waste-energy comes from the municipal waste, manufacturing
Waste and landfill gas and the alcohol fuels come primarily from sugarcane and corn and they can be used directly as a fuel or as an additive gasoline. These alcohols are mostly biodiesel or bioethanol.

In addition to fuels and power, renewable biomass resources can also be used to produce an array of energy-related products, including chemicals and other materials such as glues, cleaners, solvents, and plastics.

Figure 3.3: The cycle of the CO2 in the utilization of biomass

**Woody biomasses**

One kind of biomass is very important for my work, the woody biomasses. The most important structural materials in wood are cellulose, hemicellulose and lignin. Lignin binds the wood’s fibres together and gives the wood its mechanical strength. In wood there are also small amounts of extractives, for example resin consists of them. There are lots of vaporizing substances in wood, so its flame is long and needs a large space for combustion. The dry part in wood is about 99% and carbon, hydrogen and oxygen are the mostly elements.
Table 3.1: Elements in woody biofuels

<table>
<thead>
<tr>
<th>Element, weight-%</th>
<th>Wood</th>
<th>Bark</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>48-50</td>
<td>51-66</td>
</tr>
<tr>
<td>H</td>
<td>6-6.5</td>
<td>5.9-8.4</td>
</tr>
<tr>
<td>N</td>
<td>0.5-2.3</td>
<td>0.3-0.8</td>
</tr>
<tr>
<td>O</td>
<td>38-42</td>
<td>24.3-40.2</td>
</tr>
<tr>
<td>S</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Cl</td>
<td>&lt;0.01</td>
<td>&lt;0.01-0.03</td>
</tr>
</tbody>
</table>

The net calorific heating value of the dry matter in wood is usually 18.3-20 MJ/kg and the humidity of live wood is usually high, 40% – 60%. This makes drying an essential part of producing wood-based biofuels. It's possible to get 3 kinds of fuels from the wood: The fuel wood, the charcoal and black liquor.

The fuel wood is the traditional forest product derived from forests and trees. This kind of fuel is very used in the developing countries as a source of household energy. In Pakistan and the Philippines, for example, fuel wood covered 58 and 82% respectively.

The Charcoal is the dark grey residue consisting of impure carbon obtained by removing water and other volatile constituents from animal and vegetation substances.

The black liquor is a by-product from the paper and pulp industry. In North America and Europe, black liquors are widely used for fuelling the heat and power plants of the large pulp and paper mills. Almost all of their energy needs are met by black liquors and, in some cases, surplus electricity is sold to the public grid.

Woody Residues are currently the main sources of bioenergy and this will continue to be the case in the short to medium term, with dedicated energy forestry/crops playing an increasing role in the longer term. They are a quite under-exploited potential energy resource, and present many opportunities for better utilisation. However, there are a number of important factors that need to be addressed when considering the use of residues for energy. Firstly, there are many other alternative uses, e.g. animal feed, erosion control, use as animal bedding, use as fertilisers (dung), etc. Secondly, there is the problem of agreeing on a common methodology for determining what is and what not a recoverable residue is. As woody residues we have: Forestry residues (by-products of the pulp and paper industry), logging residues (treetops, branches and refuse logs), whole tress and stemwood, stumps, cutter chips...
3.2 SOFC fuelled with biomass

Most experiments in the actuality for the fuel cell fuelled with biofuels use bioethanol as a fuel.

On 2010, Dr. Bin Zhu and his team did, in Kungliga Tekniska Högskolan some experiments with solid oxide fuel cell fuelled with bio-ethanol and glycerol.

As electrolyte they used nanocomposite based Nano-structured on samarium-doped ceria and a second phase of $Na_2CO_3$. The cathode and the anode was a mixture of carbonates ($Li_2CO_3$, $CuCO_3$ ($OH$)$_2$, $NiCO_3$) and electrolyte.

The results of the fuel cell test with one cell were: 148 mW/cm$^2$ for the bioethanol and 215 mW/cm$^2$ for the glycerol with a very low deposition of carbon. [24]

This cell can be used for a poly-generation application at low Temperature thanks to the nanocomposite. The heat produced by the fuel cell can be used in turbine to produce further power.

This study may be very helpful for the different applications including poly-generation and hybrid system especially for transport and stationary section, because liquid fuel is very easy to carry; no other fuel cells have such kind of results with the liquid fuels.

Y. Shiratori used biogas in a fuel cell too. He used A solid oxide fuel cell with Scandia-stabilized-Zirconia (ScSZ) for the electrolyte, NiO-ScSZ for the anode and $(La_{0.8}Sr_{0.2})_0.98$MnO$_3$ -ScSZ for the cathode. At the high operating temperature of 1000 ºC with a cell voltage above 0.9 V and a current density of 200 mA/cm$^2$ was stably obtained over 50 h of performance without carbon deposition. [25]

Another kind of biomass which can be fuelled to the fuel cell is the lignin, however, the study of this device is very new and there isn’t a lot of information.

In 1984, H. Howard used sulfonated lignin and Kraft lignin as a fuel in a small fuel cell. The fuel cell consisted of two compartments separated by Pyrex fine glass frit impregnated with 2% agar dissolved in 1M of KCl. The oxidation side of the cell was maintained under $N_2$ while the reduction side was maintained under pure $O_2$ or air. The oxidation side was maintained at pH 12 with NaOH additions as necessary and the reduction side was maintained at pH 1. The results were 1 kWh for each 2-3 lb of sulfonated lignin and 5-8 lb of black liquor. [21]

In 2010, Raquel Bohn used as a fuel for fuel cell, lignosulfonate and Kraft lignin, either directly in their commercial forms, mixed with active carbon or altering their structures by a pH adjustment to pH 10. The
OCV was 0.7 V and the current density was 85 mA/cm² with the lignin mixed with active carbon and 75 mA/cm² for the lignin with pH 10. She used a direct carbon fuel cell (DCFC), the only fuel cell capable of converting solid fuel into electricity without a reformation process with low pollution. The tests were made at 550 °C and the oxidation side of the cell was maintained under N₂ while the reduction side was maintained under pure O₂ or air.[22]

![Lignin + electrolyte diagram](image)

**Figure 3.4: Fuel cell made with lignin by Raquel Bohn**

### 3.3 Lignin

#### 3.3.1 Introduction: What’s lignin?

Cotton and wood are both fibrous plant-materials that have high tensile strengths. Cellulose is a main functional compound of both, but in spite of this, the properties of the two materials are very different; cotton is soft, flexible and absorbs water up to 10 times its weight, whereas wood is a stiff material with low water adsorption. What is the chemical background to these differences?

The answer is that wood, in contrast to cotton, the wood contains large amounts of lignin (15–35 % for softwoods and around 20 % for hardwoods), a hydrophobic polymer that fills up between the cellulose micro fibrils and hemicelluloses fixating them towards each other and thus giving the cell wall its "woody" properties.

Lignin is neither a polysaccharide, a lipid, a protein, nor a nucleotide. It has the most complex structure among naturally occurring polymers with a mixture of aromatic and aliphatic moieties. It is not a linear polymer as cellulose, or a branched polymer as the hemicelluloses or pectin but rather a three-dimensional web, with the monomers (i.e., the building blocks) connected with a number of different ether (C-O-C)- and carbon-carbon (C-C) bonds that are randomly distributed, and the first impression of the covalent structure may appear chaotic.
The structure and properties of lignin are of great interest for the pulp and paper industry, since the chemical pulping and bleaching of pulp are mainly based on chemical reactions on lignin and how the lignin released during chemical pulping. Lignins are polymerized from mainly three monomers called monolignols, namely, p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. Monolignol-ratios for different lignins are shown in Table 3.2.

Figure 3.5: Lignin's structure

Figure 3.6: The monomers forming the lignin structure
Table 3.2: Compositions of monolignans in different plants

<table>
<thead>
<tr>
<th>Plant</th>
<th>p-Coumaryl alcohol (%)</th>
<th>Coniferyl alcohol (%)</th>
<th>Sinapyl alcohol (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coniferous softwood</td>
<td>&lt;5</td>
<td>&gt;95</td>
<td>None or Trace</td>
</tr>
<tr>
<td>Eudicotyledonous hardwood</td>
<td>0–8</td>
<td>25–50</td>
<td>46–75</td>
</tr>
<tr>
<td>Monocotyledonous grass</td>
<td>5–33</td>
<td>33–60</td>
<td>20–54</td>
</tr>
</tbody>
</table>

The lignin has four biological functions:

- **Lignin gives stiffness to the cell walls**: The composite nature of wood with its mixture of cellulose, hemicellulose and lignin, makes the fibers relatively stiff and rigid
- **Lignin glues different cells together in woody tissues**
- **Lignin makes the cell wall hydrophobic**: This is a prerequisite for the development of cells for efficient water- and nutrition transport
- **Lignin is a protection against microbial degradation of wood**

Lignin does not have a regular structure like cellulose, but is a physically and chemically heterogeneous material, although the exact chemical structure is unknown. [16]

### 3.3.2 History of Lignin

The history of lignin science stretches over a period of one hundred years and many scientists had made efforts effectively to exclude the lignin from wood in order to extract cellulose in the pulping process. The idea of the utilisation of the wood feedstock was exploited already in 1898 by Simonsen in his efforts to convert sawdust to ethanol. Lignin has been considered as an unwelcome by-product and attempts have been made to cultivate wood species having a small amount of lignin content using new biotechnology.

The physical chemical nature of lignin as a representative biopolymer has been neglected for a long time. Goring first shed light on the polymeric nature of lignin in early 1960. He measured the intrinsic viscosity of lignins and concluded that conformation of lignins is between an Einstein sphere and a non-free draining random coil in a solvent. He also showed that the lignosulfonate is in the form of spherical particles of a wide range of sizes according to the electron micrograph of high molecular weight fraction of sodium lignosulfonate (LS). He also reported that the softening temperature (Ts) of lignins varied from 127 to 193°C in dry state and from 72 to 128°C in moist lignins.
However, for practical approaches of effective utilization of lignins, it is important to pay attention to industrial lignins such as by-products of pulping processes and bio-ethanol production processes. In pulping processes, Kraft and sulfite pulping methods are usually used. In bio-ethanol production processes, acid hydrolysis is commonly used. [17]

### 3.3.3 Lignin as a bio-resource

Lignin is one of the most important bio-resources for the raw material of the synthesis of environmentally compatible polymers. Lignins are derived from renewable resources such as trees, grasses, and agricultural crops.

Production of lignin as a by-product of pulping process in the world is over 30 million tons per year. However, it should be noted that this value is only an estimate, since there are no reliable statistics on lignin production because it is mostly burnt as a fuel immediately after production. Commercial lignins are obtained as by-products of the pulping or bio-ethanol industries.

![Figure 3.7: Total utilization for bio-resources from wood](image)

In direct analogy to a petroleum refinery, which produces fuels and chemicals from crude oil, a biorefinery is a facility that produces multiple products, including fuel, power, and bulk or fine chemicals, from biomass. In addition, valorization of all components of lignocellulosic biomass is essential for an economically viable biorefinery. Since lignin is a principle component of biomass, the biorefinery receives and processes enormous quantities of lignin, and conversion of this component also to fuels and chemicals is imperative for economic profitability. [18]
3.3.4 Lignosulfonate

Lignosulfonates are by-products of the sulphite pulping process for the manufacture of specialty dissolving pulps and paper. The wood chips are digested with acidic calcium bisulphite for 6-10 hours at 100-300 °C in a batch-wise cooking process. During this process, the native lignin is broken down through the degradation of the randomly distributed ether bonds throughout the structure. The fragments are solubilised in the cooking liquor through covalent addition of sulfonic acid groups at various positions in the lignin structure. The sulphonic acid groups are stabilised by the presence of calcium ions.

After the competition of the cooking stage, the insoluble cellulose is separated from the solubilized lignin by filtration. Further processing of the cooking liquor involves precipitation of the sulfonated lignin through the addition of excess calcium hydroxide, the evaporation of water and residual sulfite (in the form of sulfur dioxide) and dilution with fresh water followed by ultrafiltration to remove low-molecular-weight fractions and sugar monomers. The purified calcium lignosulfonate is a pH-adjusted to a specific pH and evaporated to a dry matter content suitable for spray drying and packaging. [19]; [20]
Figure 3.9: The sulfite process

(The following structures do not specify the structure since lignin and its derivatives are complex mixtures; the purpose is to give a general idea of the structure of lignosulfonates.)

Figure 3.10: Theoretical modification of lignin in the sulphate process

The overall structure of a lignosulfonate is not known. Several models have been proposed over the years suggesting that lignosulfonate behaves as a coiled or expanded polyelectrolyte at either high or low concentration.
The by far largest utilization of lignosulfonates worldwide which accounts for as much as 90% of the worldwide production is as concrete admixtures and for energy production during the pulping process.
4 Experimental part

4.1 The Fuel cell

In this work, a low temperature solid oxide fuel cell (LTSOFC) was assembled by using Ce$_{0.8}$Sm$_{0.2}$O$_{2-δ}$ (SDC)–Na$_2$CO$_3$ (NSDC) nanocomposite as ionic conductor and LiNiCuZnO mixed with NSDC as electronic conductor.

4.1.1 Preparation of the electrolyte

The NSDC was prepared by one-step co-precipitation process. Stoichiometric amounts of Ce(NO$_3$)$_3$·6H$_2$O and Sm(NO$_3$)$_3$·6H$_2$O were mixed and dissolved in de-ionized water to form a 0.5M solution. The solution was stirred at 80°C for 30 minutes. Then a Na$_2$CO$_3$ solution of 0.5M was used as a precipitation agent. It was added into the solution with a molar ratio of (Ce$^{3+}$ + Sm$^{3+}$): CO$_3^{2-}$ = 1:2 under vigorous stirring to form a white precipitation. The precipitate was then filtrated and dried in an oven at 120°C for 12 h. Finally, the NSDC precursor was sintered in a furnace at 800°C for 4 h. The resulting material was ground completely to obtain homogenous NSDC nanocomposite powders.

4.1.2 Preparation of the electrode

The electrode was prepared mixing 1.5g of Li$_2$CO$_3$ (≥98%, Sigma–Aldrich, USA), 7 g of Ni(NO$_3$)$_2$·6H$_2$O (≥98.5%, Sigma–Aldrich, USA), 2 g of Cu(NO$_3$)$_2$·3H$_2$O (99–104%, Sigma–Aldrich, USA) and 7g of Zn(NO$_3$)$_2$·6H$_2$O (98%, Sigma–Aldrich, USA). The mixture was put in the furnace at 800°C during 4 h. The resulting material was ground completely to obtain homogenous LiNiCuZnO powder.

4.2 Treated lignin as a fuel

In order to achieve a better performance and conductivity of the fuel cell, the lignosulphonate was treated with some hydroxides/chlorides. Then the treated lignin was sintered at different temperatures (200 -500 °C) in the laboratory furnace. The detailed of the treated lignin for my experiments was described as below.
4.2.1 Treatment with Iron chloride
It has been demonstrated that the doped sulfur lignin has the properties of a semi-conductive polymer. The conductivity of the sulfonated lignin is $1.2 \times 10^{-10}$ S/cm, but after doping with FeCl$_3$, its conductivity increased as 0.006 S/cm. [27]
Using the same idea, I used 5ml solution of Iron chloride (FeCl$_3$) and mixed with 1 g of lignin in a crucible and covered with aluminum foil. Then the sample was heated in the furnace for one hour at different Temperatures (200 – 500 ºC). The obtained dried powder/material was ground completely.

4.2.2 Treatment with hydroxides
In order to compare the results of different treated lignin, the lignin was treated with hydroxides too. The 0.4 g of NaOH was mixed in the 100 ml of de-ionized water to get a solution. The 8g of lignin was used in a 80ml solution of the hydroxide. The sample was dried at 150 ºC for 24 hour. After that, this dried powder was divided in 4 parts and sintered each part at different temperatures (200, 300, 400, 500 ºC) using the aluminium covered crucible to avoid the the oxidation. To get the homogenity of the sample, the resultant powder was ground in a mortar.

4.3 Lignin Fuel cell Fabrication
Two kinds of fuel cell was made for measurements using treated lignin.

i. three component fuel cell
ii. single component fuel cell

4.3.1 Three component fuel cell
The pure lignosulfonate was tested with a conventional three component fuel cell (Anode-electrolyte-Cathode). The electrolyte used on the cell was SDC. The Anode was a mixture of lignosulphonate with LiNiCuZnO and SDC with the same volume ratio, the cathode was a mixture of LiNiCuZnO with SDC also with the same volume ratio.
For the treated lignin, a conventional fuel cell was fabricated with three layers: Anode-Electrolyte-Cathode using a layer of lignin which acts as a fuel layer.
The electrolyte used in the cell was pure NSDC and the layer which acts as fuel was a mixture of lignin treated with pure sulfonated lignin, electrolyte and electrode with a volume ratio of $Lignin$ treated: pure $lignin$ electrode:electrolyte $= 2:2:1:1$.
The layer of Anode and Cathode was the same, a mixture of electrode and electrolyte with the same volume ratio. In each case, the Anode side was covered with Nickel foam and the cathode side was painted paste with silver, both used as a current collector. To build the cell with lignin sintered at 400 ºC and 500 ºC, I had to mix it before with binder to have a good mechanical strength.
The diameter of the cell was 1.3 cm, the thickness was 0.15 cm and the active area was 0.64 cm². The schematic structure of the prepared cell is shown in figure 4.1

![Diagram of a three-component fuel cell with lignin treated](image)

**Figure 4.1: Three component fuel cell with lignin treated**

### 4.3.2 Single component fuel cell

I also tried to use lignin in a single component fuel cell which is recently introduced by our group. The single component was a mixture of treated lignin with pure sulphonated lignin, electrode and electrolyte. The volume ratio of the single layer was:

Lignin treated: Pure lignin: electrode: electrolyte = 2:2:1:1

One side of the cell was covered with Nickel foam and the other side was pasted with silver, both used as a current collector. To build the cell with lignin sintered at 400 and 500 °C, I had to mix it before with binder to have a good mechanical strength.

The diameter of the cell was 1.3 cm and thickness 0.1 cm and using the active area 0.64 cm². The schematic structure of the single component cell is shown in figure 4.2

![Diagram of a single component fuel cell with lignin treated](image)

**Figure 4.2: Single component fuel cell with lignin treated**

### 4.3.3 Dry press method

Dry power press method was used for the preparation of cell pellet. With this method it was possible to attach the different layers of the fuel cell from the powders of each used materials. The pressing power require for the manufacturing of fuel cell is 25 Mpa. Before testing, the cell I painted the cathode side with silver paste to improve the electrical contact.
4.4 Fuel cell test

Testing device consist of two u-shaped pipes. The fuel cell was fixed in the device, and one of the two pipes was used for the transportation of air to the cathode side. Here, the fuel is attached in the anode side.

For the test, the device was put in the furnace and heats it up to require temperature. The fuel cell was measured at 550 °C under a variable resistance load, which adjusts the outputs of cell voltage and power. The values of the voltage and current were recorded by using the fuel cell testing unit (L43-China). The
test takes almost 15 minutes. After collecting data of the cell voltage and current under each resistance load, current density-V (voltage) or current density-P (power density) curve was drawn from the calculation results using the collected data.

![Figure 4.5: Furnace used for the fuel cell test with and without the device](image)

### 4.5 X-ray diffraction test

In order to know more about the structure of lignosulfonate and the treated lignins I did and X-ray diffraction test in the chemical department of Kungliga Tekniska Högskolan.

Powder X-ray diffraction (XRD) patterns of the samples were collected on a Philips X-ray Diffractometer with Cu Kα radiation (λ = 1.5418 Å) for phase analysis. With this technique, it’s possible to see if the lignin presents some crystal structure or not.

### 4.6 Conductivity measurements

To know more about the lignin, the conductivity of the lignin was measured with the VersaSTAT potentiostat machine connected to a computer. For this, I made a pellet of pure lignin only by the dry press method. To build the pellet with lignin sintered at 400°C and 500°C, I had to mix it before with binder to have a good mechanical strength. Each pellet was painted in both side with silver paste, which plays the role of current collector, and the pellet was put in the cylindrical furnace. I measured the conductivity with the help of the machine and I recorded the impedance results in a computer thank’s to the VersaStudio Software. The measurements were made it at 500 and 550 °C due to that the resistance of the lignin at low temperature was very high.
5 Results and discussion

5.1 Fuel cells performance

5.1.1 Lignosulfonate (Three component)

The fuel cell test was made with a fuel cell with 3 layers. The anode was a mixture of lignosulfonated with LiNiCuZnO and SDC and the cathode was a mixture of electrode and electrolyte at 50 % of volume. Also Ni foam was put on the anode side of the cell and I painted with silver painted the cathode side to enhance the conductivity. The Open circuit voltage (OCV) was 0,09 V at 550°C, the maximum current density at these temperatures was 11 mA/cm² with an area of 0,64 cm².

The results were very bad, that’s why I decided to do some treatments to the lignin.

5.1.2 Lignin treated with hydroxides (Three component)

The fuel cell test was made with a fuel cell with 4 layers. One of the layers is a mixture of lignin treated with hydroxides, pure lignin, NSDC (electrolyte) and LiNiCuZn (electrode) with this ratio: 2;2;1;1. This layer is attached to a three component fuel cell, I mean, a conventional fuel cell constituted of Anode, electrolyte and Cathode. The anode and the cathode have the same constitution, a mixture of electrode and electrolyte at 50 % of volume. Also I put Ni foam on the anode side of the cell and I painted with silver painted the cathode side to enhance the conductivity.

I tested the lignin sintered at 4 different temperatures (200, 300, 400 and 500 °C). The results and the operating conditions are shown in the table below:

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
<th>Operating temperature (°C)</th>
<th>OCV (V)</th>
<th>Current density (mA/cm²)</th>
<th>Power density (mW/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell A</td>
<td>200</td>
<td>521</td>
<td>0,23</td>
<td>78,12</td>
</tr>
<tr>
<td>Cell B</td>
<td>300</td>
<td>546</td>
<td>0,2</td>
<td>46,87</td>
</tr>
<tr>
<td>Cell C</td>
<td>400</td>
<td>542</td>
<td>0,074</td>
<td>67,18</td>
</tr>
<tr>
<td>Cell D</td>
<td>500</td>
<td>480</td>
<td>0,42</td>
<td>132,81</td>
</tr>
</tbody>
</table>
Figure 5.1: Performance of Cell A

Figure 5.2: Performance of Cell B

Figure 5.3: Performance of Cell C
In this case, this kind of lignin gives better results than the pure lignin. Especially the lignin sintered at 500 °C due to the carbon layer made by the sintering.

5.1.3 Lignin treated with Iron chloride (Three components)

The fuel cell test was made with a fuel cell with 4 layers. One of the layers is a mixture of lignin treated with hydroxides, pure lignin, NSDC (electrolyte) and LiNiCuZn (electrode) with this ratio: 2;2;1;1. This layer is attached to a three component fuel cell, I mean, a conventional fuel cell constituted of Anode, electrolyte and Cathode. The anode and the cathode have the same constitution, a mixture of electrode and electrolyte at 50 % of volume. Also I put Ni foam on the anode side of the cell and I painted with silver painted the cathode side to enhance the conductivity.

I tested the lignin sintered at 4 different temperatures (200, 300, 400 and 500 °C). The results and the operating conditions are shown in the table below:

Table 5.2: Performance and operating conditions of the cells

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
<th>Operating temperature (°C)</th>
<th>OCV (V)</th>
<th>Current density (mA/cm²)</th>
<th>Power density (mW/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell A</td>
<td>200</td>
<td>415</td>
<td>0,126</td>
<td>59,37</td>
</tr>
<tr>
<td>Cell B</td>
<td>300</td>
<td>415</td>
<td>0,195</td>
<td>46,87</td>
</tr>
<tr>
<td>Cell C</td>
<td>400</td>
<td>480</td>
<td>0,08</td>
<td>0</td>
</tr>
<tr>
<td>Cell D</td>
<td>500</td>
<td>500</td>
<td>0,183</td>
<td>48,43</td>
</tr>
</tbody>
</table>
Now, this kind of lignin gives better results than the pure lignin but worse than the lignin treated with hydroxides. Here, the lignins sintered at 200 °C and 300 °C give the best performance.
5.1.4 Lignin treated with hydroxides (Single component)

In this case, the fuel cell test was made with a Single component. This cell was made only with one layer constituted by a mixture of lignin treated with hydroxides, pure lignin, electrolyte (NSDC) and electrode (LiNiCuZn). Also, in on side of the cell I put Nickel foam and in the other side I painted with Silver paste. I treated the lignin sintered at 4 different temperatures (200, 300, 400 and 500 °C). The results and the operating conditions are shown in the table below:

<table>
<thead>
<tr>
<th>Sintering temperature (°C)</th>
<th>Operating temperature (°C)</th>
<th>OCV (V)</th>
<th>Current density (mA/cm²)</th>
<th>Power density (mW/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell A</td>
<td>200</td>
<td>0,484</td>
<td>82,81</td>
<td>16,15</td>
</tr>
<tr>
<td>Cell B</td>
<td>300</td>
<td>0,48</td>
<td>81,25</td>
<td>8,59</td>
</tr>
<tr>
<td>Cell C</td>
<td>400</td>
<td>0,35</td>
<td>73,43</td>
<td>6,73</td>
</tr>
<tr>
<td>Cell D</td>
<td>500</td>
<td>0,345</td>
<td>156,25</td>
<td>8,73</td>
</tr>
</tbody>
</table>

Table 5.3: Performance and operating conditions of the cells

Figure 5.8: Performance of Cell A
With the single component device I get the best results, especially with the lignins sintered at 500°C due to the carbon layer.

The OCV in this case is higher than the others experiments. This can be due to the ohmic losses. With a device with three components the ohmic losses can be higher than this cell where we only have one component.
5.2 XRD results

In the figure 5.12 are shown the results of the XRD made of the 5 kinds of lignin treated with hydroxides, the lignosulfonate (pure lignin) and the active carbon.

The result of the pure lignin can confirm that is not an inorganic compound, is an organic compound, because it has an amorphous structure. Also, all the results have one thing in common, the peak of the carbon structure at 24 degree.

It's normal too to see the differences between the pure lignin and the other lignin. The lignins sintered at 100, 200 and 300 ºC present peaks at 31, 38 and 48 degree of NaOH and at peak at 32 degree of KOH. Of course this is very normal because we treated before with KOH and NaOH.

I noticed that the peaks disappear when the lignin is sintered at 400 or 500ºC. However, new peaks appear after this at 29, at 32, at 34, and 57 due to the formation of KNaCO$_3$ at 400 and 500ºC by this way.
The KNaCO$_3$ is present as a crystal structure, but maybe, it can stay as an amorphous structure too. This could explain why, with the lignin sintered at 500°C we have a good performance. An amorphous structure of KNaCO$_3$ can increase the ionic conductivity because it can produce an interphase between the electrolyte and the KNaCO$_3$. [26]

Also, if I see the results from 64 to 80 degree I can note that the form of the curve of lignin is similar to the pure active carbon. That’s because the lignin sintered at high temperature had covered with a layer of carbon. We can think that also this layer of carbon gives good values of OCV and current because the lignin sintered at 500°C gives the best performance.

Figure 5.13: XRD results of lignin treated with Iron chloride

The results of the XRD of the lignin treated with Iron chloride are shown in the figure 5.13. If I compare
this kind of lignin with the other one I can see that the structure of this lignin is not so amorphous like the other one. This is due to the structure of the Iron chloride.

I can see with the peaks at 33 and 55 degree that the lignin sintered at 400 and 500 °C presents some traces of Fe$_2$O$_3$ and FeClO. Maybe, I get this with this reaction:

$$\text{FeCl}_3 + \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + \text{FeClO}$$

$$2\text{Fe(OH)}_3 + \text{FeCl}_3 \rightarrow 3\text{FeClO} + 3\text{H}_2\text{O}$$

Maybe, that’s why the lignin sintered at 200 °Chas the current density, because they have a big amount of FeCl$_3$ in comparison with the others lignin and this enhanced the conductivity.

### 5.3 Conductivity Measurements

In the next table I show the results of the conductivity tests of lignin treated with Iron chloride:

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Type of lignin</th>
<th>Temperature in °C</th>
<th>Resistance in Ω</th>
<th>Conductivity (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,5</td>
<td>100 F</td>
<td>500 530</td>
<td>5 0,17</td>
<td>500 530</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5 100 F</td>
<td>0,17</td>
<td>4,6875 137,8676</td>
</tr>
<tr>
<td>1,5</td>
<td>200 F</td>
<td>545 500</td>
<td>31,3 60</td>
<td>545 500</td>
</tr>
<tr>
<td></td>
<td></td>
<td>545 500</td>
<td>500 545</td>
<td>0,748802 0,390625</td>
</tr>
<tr>
<td>1</td>
<td>300F</td>
<td>500 545</td>
<td>900 211</td>
<td>500 545</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500 545</td>
<td>500 545</td>
<td>0,017361 0,074052</td>
</tr>
<tr>
<td>0,8</td>
<td>400F</td>
<td>500 550</td>
<td>310 90</td>
<td>500 550</td>
</tr>
<tr>
<td></td>
<td></td>
<td>500 550</td>
<td>0,040323 0,138889</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>500F</td>
<td>510 560</td>
<td>127 33</td>
<td>510 560</td>
</tr>
<tr>
<td></td>
<td></td>
<td>510 560</td>
<td>0,123031 0,473485</td>
<td></td>
</tr>
</tbody>
</table>

The lignin sintered at 100 °C and treated with Iron chlorides gives the best conductivity. I think the reason is that this lignin has a good amount of Iron chloride and no other compounds like Fe$_2$O$_3$ or FeClO and also this Iron chloride gives a good conductivity to the lignin. Also, we have good values with the lignin sintered at 200 °C, for the same reasons, and at 500 °C. At 500°C, the lignin doesn’t have much Iron chloride like the others lignins, but, with the sintering, this lignin has obtained a layer of pure active carbon which gives a good conductivity.
So, the reason that I have the best current density with the lignin sintered at 200 °C (as you can see above in the results of the fuel cell tests) can be the presence of the Iron chloride.
The treatment was successful because the conductivity is higher than the pure lignin.

In the next table I show the results of the conductivity tests of lignin treated with hydroxides:

<table>
<thead>
<tr>
<th>Thickness</th>
<th>Type of lignin</th>
<th>Temperature in °C</th>
<th>Conductivity (S/m)</th>
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I can see that the lignin which has the best conductivity is the lignin sintered at 500°C. This should be normal because as is shown in the XRD results this kind of lignin has a layer of activated carbon, and also maybe it has KNaCO₃ as amorphous structure, which gives good values of conductivity. The worse value of conductivity is given by the lignin sintered at 100°C. This is because, at this sinter temperature, the lignin didn’t make the carbon layer like the lignin sintered at high Temperature.

If I compare the conductivity results with the results of the fuel cell test it’s possible to see that they are related. I obtained good results of current density with the lignin sintered at 500°C to both three components and single component.

Here the results were successful too. With the treatment the lignin has more conductivity than before.

If we compare the two treatments, the lignin treated with hydroxides gives better results than the lignin treated with Iron chloride. This can be due to the relation between the lignin treated with Iron chloride and the mixture of electrolyte and electrode, or, maybe the problem is that there are some interactions between the iron chloride and the carbon which is the fuel. This hypothesis can be solving with an IR test to see the functional groups of the lignin treated with Iron chloride.
Also, the lignin treated with Iron chloride which has a pH lower than the lignin treated with hydroxides, so, is more hydrophilic. The hydrophilicity is a critical factor for the fuel cell performance. If one compound is more hydrophilic than other, the performance of the cell will be worse because the electrolyte of the SOFC works bad with the presence of water. This can be a reason of the good results gave by the experiments with the lignin treated with hydroxides.

5.4 Fuel cell efficiency

I will calculate the electrical efficiency of the cell with the higher value of current, the cell D of the single component (E= 0.304 V ; I= 53.18 mA/cm² ; P= 16.15 mW/cm²). To calculate the efficiency, we have to follow the system of the photo. I don’t know exactly if the fuel used in the fuel cell is mostly carbon, but I assume that is true. Is necessary to do some studies in the future to see if this model is true.

**Electrical efficiency**

Anode reaction:  \( C + 2O^{2-} \rightarrow CO_2 + 4e^- \)

Cathode reaction: \( O_2 + 4e^- \rightarrow 2O^{2-} \)

Overall reaction: \( C + O_2 \rightarrow CO_2 \)

The electrical efficiency is: \( \varepsilon = \frac{-nFE}{\Delta H} \)

**Thermal Heat** = \( \varnothing H = \sum H_{Produced} - \sum H_{Reaction} \)
\[ H_{O_2} = \Delta H_{fO_2} + C_p \left( T_2 - T_1 \right) = 0 + 29,35 \times (550 - 25) = 15408 \frac{J}{mol} \]

\[ H_{CO_2} = \Delta H_{fCO_2} + C_p \left( T_2 - T_1 \right) = -393509 + 37,11 \times (550 - 25) = -374081 \frac{J}{mol} \]

\[ H_C = \Delta H_{fC} + C_p \left( T_2 - T_1 \right) = 0 + 8,527 \times (550 - 25) = 4476,6 \frac{J}{mol} \]

\[ \Delta H = H_{CO_2} - H_{O_2} - H_C = -374081 - 15408 - 4476,6 = -393965,6 \frac{J}{mol} \]

The electrical efficiency is:

\[ \varepsilon = \frac{-nFE}{\Delta H} = \frac{-4 \times 96485 \times 0,304}{-393965,6} \times 100 = 30\% \]

It couldn’t be possible to calculate the heat efficiency of the fuel cell because we need to know a lot of things about the lignin to continue. I don’t know exactly which the products of the lignin are after burning at 550 °C and the heat values of the lignosulfonated. Of course, this has to be done in the future to continue the studies.
6 Conclusions

It has been demonstrated with this project that the solid biomass can be used as a fuel for the Solid Oxide Fuel Cell for polygeneration applications (Combined heat and power generation) using nanocomposites materials to work at low Temperature. This is very important for the waste management of lignin in the paper manufacturing.

The treatments made to the lignin were very successful. The conductivity and fuel cell performance in each case increase if we compare with the pure lignin.

Also, with this kind of fuel cell is possible to use a renewable energy to reduce the amount of CO$_2$ in the atmosphere with an electrical efficiency of 30 % and a power density of 16 mW/cm$^2$. The best way to use it is doing a treatment with hydroxides before.

It’s also possible to use the lignin with the new Single component fuel cell with a very good performance.

However, the study doesn't finish here. The electrical efficiency or the power density of the fuel cell can be improved if we change some parameters in the experiments like, for example, the quantity of FeCl$_3$ in the treatment, the pH of the lignin, the ratio in the fuel layer or in the electrolyte…

Also is very important to know more about the behaviour and the structure of lignin in order to improve the results and calculate the thermal efficiency. We should do some IR, SEM and TEM test to study the structure of the pure lignin and the treated lignin. To do some experiments in order to know all the important products in the combustion of lignin and it heat values.

This project makes the LT SOFC more applicable in different fields as compared to others fuel cell.
7 Bibliography


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Biopolymers. Lignin, Proteins, Bioactive Nanocomposites


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