Direct Solar-to-Fuel CO$_2$ Reduction

BY

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THESIS

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To my Family.
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SUMMARY

One of today’s main scientific development topics is about satisfying the rising energy demand in an environmentally friendly way. Observing the present global scenario and analyzing the different solutions for this problem, we tried to provide an answer to this urgent problem.

Reducing CO2 emissions in the different energetic processes is the first requirement emphasized in this global debate. In the environmental discussion often hydrogen has been proposed as the ideal fuel but, even if hydrogen is the simplest element in the periodic table, the most abundant one, with a good energy content and reactivity and could seem a completely green fuel, today’s H2 production is mostly environmentally un-friendly. In fact not everything about Hydrogen as the new fuel is positive: even if there is plenty of hydrogen around it takes large amounts of energy to strip it free because it’s mostly bound with other atoms in complex molecules and since it usually needs extra energy to get separated most hydrogen today is made from the usage of fossil fuels, releasing vast quantities of carbon dioxide in the process and so going exactly against the initial purpose.

So, definitely this is neither the way or the fuel that we are looking for to solve our energy problem without contributing to the GHG issue.

In this work we try to provide a new solution to the energy problem. Capturing and reducing CO2 to produce syngas (CO + hydrogen) using just the Sun as an energy source could be the right path in figuring out the problem. In this way it will be possible to produce
hydrogen and, in the mean time, literally reduce CO2 in a completely “green” way. In fact the out-put products of our system are hydrogen and CO, which together form syngas, and O2. Syngas is a combustible gas that can be easily recombined to form several types of fuel such as gasoline or methane. In addition to that we know that burring H2 or syngas like a classic internal combustion engine’s fuel is not the only option: recombine Hydrogen with Oxygen in a fuel cell and you will produce clean water and electricity, without the fossil fuels’ noxious pollutants. The global calculation has shown that, even saving all the energy that we already use, we are going to need 16 more TW before 2050 so we need a new effective source of energy to store into a fuel.

Sunlight could be the only source capable, all alone, of replacing fossil fuels, meeting the rising global energy demand in a renewable and carbon-neutral energy way. But the challenge is not yet solved: the day-night difference in insolation and the diurnal variation in local insolation requires an efficient and cost-effective storage method in order to transform the sunlight into the new main large scale energy source. The best way to store the sun’s enormous potential is in chemical bonds. Among the variety of different storage methods, nature provides the most effective and better engineered blueprint for storing sunlight in the form of chemical fuels [12]. In fact, in natural photosynthesis, sunlight’s energy is used to rearrange the bonds of water to oxygen and hydrogen equivalents.

Based on several studies, we have tried to understand the best direction to follow and all the tools that science and nature offer us selecting the solution that seems the best from the scientific and social/economic point of views.
Inspired by two main research studies: the batch and continuous flow CO2 reduction from Prof. Salehi’s research group (UIC) and the direct water-splitting from Prof. Nocera’s research group (MIT), we describe and perform the development of a cell for a direct-photo CO2 reduction and a direct-photo-water splitting comprising earth-abundant elements which operate in controlled conditions.

The system consists in coupling the OER-catalyst, developed at MIT, and the CO2 reduction cocatalyst system, developed at UIC, into a unique design that photo-activates the two semi-reactions by the photo-excitation of an amorphous silicon triple-junction designed to generate about 1.8 V of built-in potential. The final goal of this work is to attempt to close the loop of combustion: burning fuel we obtain energy and waste products, most of which is CO2; the idea is to take this waste product of combustion and, using a totally green source of energy, the sun, retransform it back into fuel, closing the loop of combustion.

Figure 1. Scheme of the cycle that we attempt to reproduce.
CHAPTER 1

INTRODUCTION

In this chapter the global energy problem will be discussed putting the major focus on future prospectives. Starting from an estimation of the future global energy need, the issues related to the rising level of CO2 in the atmosphere and the constant and growing demand for energy will then be discussed. In order to have the best picture of the problem, in this chapter we also include an estimation of solving the future enormous need of energy using the current energy production methods such as nuclear, biomass, wind, hydroelectric and fossil fuel.

After describing this scenario the only resource left out will be investigated: the sun. First we clarify the potential of solar energy, its issues are then analyzed. The major problem with solar is storing efficiently its enormous potential and the best solution found is to embed its energy in chemical bonds: sun-to-fuel.

The best example to follow in order to achieve the goal of carbon neutral efficient and green source of energy is natural photosynthesis.

In the end of the chapter a possible analogy in collecting sun energy between nature and technology with a complete comparison of efficiency is underlined. In this way a starting point and a new challenge is set clear.
1.0 **Initial Reflection**

Proved as the major cause of the ‘‘greenhouse effect’’ CO2 has become the centre of concern for the scientific community. The common goal of both government and scientists is to find a solution for this emerging problem via simultaneously minimizing CO2 emissions and selecting a new green energy source.

Proof of this international commitment is the Kyoto Protocol which was enacted and subscribed by many countries. Since fossil fuels are a major source of CO2 emissions, the European Union, first among the others, has been seeking to promote the use of biofuels or other “greener” technologies as substitutes for diesel or petrol in order to contribute and fulfill the promises previously pledged on the topics of environmentally friendly energy supply, climate change and promotion of renewable energy resources.

The US policy is not much different; even though the US government hasn’t fixed such definite aims as the EU it can be asserted that the need for alternative CO2 free fuel is worldwide a primary issue. In the US, transport has one of the biggest environmental impacts because of the consumption of large amount of energy in the form of fossil fuels.

Figure 2 identifies total 2004 U.S. energy emissions by sector. As underlined before it is seen in the figure that the greatest quantity of emissions of GHGs come from industry and transportation, at 30 and 28 percent of total emissions, respectively [10]. It has been predicted that the continued use of fossil fuels in a similar structure, will ensure that the carbon dioxide level could easily double by the end of the 21st century [10].
1.1 GLOBAL CALCULATIONS: Energy Consumption

In order to better understand how to solve this problem, it is essential to understand the energy requirements for the future. For this objective, first we need to define a unit: TW. The Tera-Watt (TW) is not an energy unit, it is power \((10^{12} \text{ Watt “light bowl”})\), power is energy per unit time and that’s the easiest and most practical unit to truly understand our rate of energy consumption \((E’\)).

![Global energy inventory](image)

Figure 3. Global energy inventory \([6, 39]\).
Figure 3 shows an estimation of energy consumption. In 2000, we were burning a 12.8 TW. Looking at the graph we can clearly see that almost all the energy (10 out of 13 TW) that powers our “Earth-light bowl” comes from oil gas and coal, all resources that inexorably increase the CO2 level in the atmosphere. In the year 2050 we can estimate that we are going to need about 28TW [6]. To make this estimation Prof. Nocera and Lewis only used three fundamental factors:

- How many people will be on the planet: global population (N)
- Globally averaged gross domestic product (GDP) per capita (GDP/N)
- Globally averaged energy intensity (energy consumed per unit of GDP) : (E’/GDP)

\[
\dot{E} = N \cdot \frac{GDP}{N} \cdot \frac{\dot{E}}{GDP}
\]

The world population was 6.1 billion in 2001 and is projected to increase by 0.9% per year getting to 9.4 billion by 2050. World per capita GDP was $7,500 per capita in 2001 and it is projected to increase at the historical average annual rate of 1.4% reaching $15,000 per capita by 2050[6].

Without variations of the globally averaged energy intensity, because of population
and economic growth, the world energy consumption rate would grow by 2.3% yr⁻¹: from about 13 TW in 2001 to about 40 TW in 2050 [6]. Anyhow it is important to consider that the global average energy intensity has inexorably declined in the past 100 years thanks to technological improvements throughout the energy production, distribution, and use. So, even taking into account this reduction considering a grow of 1.5% per year, it has been estimated that the world energy consumption rate will double from 13.5 TW in 2001 to 27 TW by 2050 and triple to 43 TW by 2100 [6].

We have to remember that in only an hour 204,000 people will be born into the world and our energy need strictly depends on that, plus the global average of GDP (2.3%) which is probably correct but emerging countries like China have grown at 6.6% and they have also reached 10-12% [6].

We need also to underline that in this prediction it’s assumed that we are going to have 100% conservation of the energy we are currently using, so basically it has been assumed that we will save all of the 13 TW we are using today until 2050 otherwise another 27 TW will be needed by 2050. Here it has been plotted GDP and how much energy we use per person graph to better understand how energy management influences our life [6].
Analyzing this plot we have also to take into account that the U.S. is not the “worst” county among the majors, in terms of energy demand per GDP; this plot is not big enough to represent them all, there are at least 13 other country “worse” than the US. Good news: if a country (i.e. U.S.) has a horizontal orientation that means they have a very good energy intensity. Therefore, they don't need more energy to make GDP grow.
If we want to understand the standard of living that we will have in the future to solve the energy problem with just 30 TW we have to think that the entire world should have the same standard of living that Equatorial Guinea has now. If we want to do the estimation with the U.S. standard of living we are going to need 102.2 TW; that tells us how much conservation we are going to need. It also needs to be said that, especially in the short term, according to statistics, we are not running out of fossil fuel resources. This generation will probably never see the earth without oil, coal and natural gas. If this generation would only worry about running out of these resources, the people now on the earth would not worry about anything but a little bit of energy price growth but the things are not quite like this because of CO2 raising (and I will explain the reason later). Right now we still have:

- 200 years of oil (Saudi Arabia)
- 400 years of natural gas (Russia)
- 2000 years of coal (we can make any hydrocarbon with just coal)

So at the end of the day the real issue is the CO2 problem; so if we don't believe in climate change and pollution we shouldn't have any problems [6]. Instead, in the next few years, because of CO2 the environment will become more and more inhospitable.
1.2 **MAIN ISSUE: the unacceptable level of CO2**

The real issue about powering the new world is the increase in CO2. If we want to give the future generation the possibility to inhabit this planet in the future we need to find a carbon neutral sustainable energy resource.

![Figure 5. Total anthropogenic GHG emissions (GtCO2eq/yr) by economic sectors [4].](image)

As we can clearly see from the previous figure, almost all the GHG emissions are due to transportation, industry and electricity generation and heating [4].
According to the graph in Fig 6 it’s easy to see that the trend on CO2 concentration has almost constantly raised in the past 50 years [4].

The data indicates that we are just putting more than 2% of C more every year and what that means is that a mass of carbon flux is coming into the atmosphere. To understand
how much this perturbation could affect us we need a numerical example: if our starting number is 200; with an annual increment of 2% the second year it becomes 204, in 40 years it will be more than 440.

Figure 7. CO2 vs Temperature: a Snapshot/100000 yr trend [39].

So now the upcoming question is:

*How can we be so sure that the raising of CO2 is directly connected to us burning fuel?*

Changing the perspective, as is seen in Fig 7, we have the opportunity to see that the correlation between temperature and CO2 concentration could be faked only if we just
analyze a short period of time but analyzing from the right perspective it is unequivocal that CO2 and the temperature level are strictly correlated.

The C level in the atmosphere has never been above a 315 ppm for 650,000 years and that’s a scientific fact but it’s also a fact that when it was above 315 ppm there weren’t six billion people trying to survive on the Earth, it was a completely different-looking world.

So finally we have to conclude that the real issue is our inappropriate use of fossil fuel and especially the CO2 content directly consequent to this use.

- From coal (2 H2 per each CO2 produced): C + 2H2O→CO2 +2 H2
- From methane (natural gas) (4 H2 per CO2): CH4 + 2 H2O→CO2 + 4 H2

So methane is twice as good as coal. The quantity of H produced could be a great parameter to compare fuels since hydrogen as a fuel, is the cleanest. and because of that we have to emphasize that using Fischer–Tropsch processes we can convert syngas into methane or methanol or other fuels with a very high content of Hydrogen. So from this consideration we can conclude that the first thing we need to do is cut our tie with C.
1.3 SOLVING THE PROBLEM WITH CURRENT TECHNOLOGIES

In order to better understand how to solve this problem in this chapter an estimation is made of solving the future enormous need for energy with today’s way of producing energy such as nuclear, biomass, wind, hydroelectric and fossil fuel.

Figure 8. Energy estimation prospectives [6, 39].

Using our actual technology we can try to estimate how to satisfy the future energy need.
Leaving the coal, oil and gas base of around 10 TW we can make some assumptions about how we will overcome the energy problem in the future investigating the different options that we have to fulfill the 16 TW and more, supposing 100% of conservation, left to be found.

Considering the present alternative energy resources in the world that we could expect, continuing without changing anything the present way to produce and distribute energy, it should look like this:

- All the plants on the face of the earth are just used for biomass with the only exception of the ones that provide our 2000 cal a day to collect 5-7 TW.
- A new nuclear power plant every 1.5 days to collect 8 TW
- Windmills everywhere on the face of the earth (10 m above the ground 2.1 TW; 100 meters above the ground 4.5 - 5 TW)
- Every river dammed to collect 4-6 TW through hydroelectric energy production

That's what the earth will look like unless we find a new way to produce and store energy [6].

The only resource that we haven't talked about is the one that, as has been mentioned before, the one that has always powered the earth and ourselves and the one that we receive in abundance every single day: solar energy (120,000 TW). So basically
all that we need to do is to find a way to store all of this solar energy that the sun continuously gives us freely even on the most cloudy day.

1.4 THE SOLAR RESOURCE

Sunlight is without any doubt the most abundant and sustainable source of energy available to humanity. Our planet receives no stop irradiation from the sun at the rate of approximately 120,000 TW (1 TW = 1012 W) almost homogeneously distributed allover earth surface [13]. This total quantity largely exceeds the total annual energy-consumption-rate of about 15 TW furthermore any conceivable future needs stays within this range. Even if the source now is clear the challenge is not completely solved because, despite the abundance of sunlight energy this is distributed in a very “dilute” fashion. In fact every year the average solar power which strikes the Earth’s surface is about 170 W per square meter, quantity that varies according to latitude and geographical location. [13].

1.4.1 What's the problem with solar?

Now solar is only 0.1% of the market for two main reasons:
- Photovoltaic is too expensive; 5 years ago they were $8 square-foot now $28-$25: it’s still much cheaper to use coal at 3-5 cent/KW (not only because solar is too expensive but coal is too cheap)
- if you can’t store it efficiently you are not going to use it because you can use it only when the sun is up.

Figure 9. Demand-Solar Generation Mismatch [39].

So the challenge becomes the storage of this abundant source of energy. The more efficient way to store energy, which has already been proved, is in chemical bonds; that’s why fossil fuels work so well. Nature has given us the best example of the mechanism that stores sunlight energy into chemical nutrients: photosynthesis.
1.5 **CONCLUSION**

Our planet’s current energy needs are 14 TW; we are going to need 16 TW by 2050 because there are going to be 6 billion new energy users. But the real issue about powering the new World is the increase in CO2; so we need to find a carbon neutral sustainable energy source if we want not only to power the world but also to give the future generations the opportunity to live there. In fact, proven as the major cause of the “greenhouse effect”, CO2 has become the center of concern for the scientific community choosing, as the common goal of both government and scientists, the idea that the emissions of this gas should be minimized.

The only resource abundant enough and potentially completely carbon free is the same one that has always powered the Earth and ourselves: solar energy (120,000 TW). But with this affirmation another issue is raised: an efficient and carbon neutral way to store it. Basically all what we need to do is find a way to store all of this solar energy that the sun continuously gives us freely even on the most cloudy day and the best way to do so is to capture it in chemical bonds creating a solar made fuel, exactly what plants do in photosynthesis. In order to replicate this mechanism it’s important to compare the difference between the natural and the artificial photo-system. It can be concluded that further productivity gains in both photosynthetic and PV systems can be achieved by resetting the limits to energy conversion via a new designed systems.
CHAPTER 2

POSSIBLE SOLUTIONS

In order to better choose a solution to the energy problem we have to take into account several factors. Deeply understanding what a fuel really is and what solar-to-fuel energy production means is a fundamental step in this process. In this chapter the requirements and the features of an energy vector will be discussed. Furthermore there will follow an analysis of today’s favorite candidates and their pros and cons. The chapter will be concluded with our final fuel suggestions and the best example to follow in order to achieve a carbon neutral efficient and green source of energy: natural photosynthesis.

2.1 WHAT WILL THE FUEL OF THE FUTURE BE?

From the above discussion we can conclude that the fuel of the future cannot be linked in any way to oil or the fossil fuel economy; it has to be CO2 emission free, easily and cheaply produced on a large-scale, which means energy possibly produced “in loco”, where and when it’s needed.

Is important to underline also that the development cycles of technologies that employs materials difficult to produce and manufacture tends to be long to develop and
implement. On the other hand discoveries founded on a straight-forward-easy production and earth-abundant materials makes the manufacture and implementation faster and so this type of technologies can have much shorter iterative development cycles [5].

From all the possible solutions, in recent decades, the scientific community has always pushed hydrogen as one of the most efficient and valuable alternatives as energy vector but H2 alone cannot solve the problems connected to the rising of CO2. Most hydrogen today is made from fossil fuels, releasing vast quantities of carbon dioxide in the process. That’s why in this project we propose a way to couple the benefits of H2 with a CO2- emission-recycle-system that reconverts the unused main product of combustion (CO2) into fresh usable fuel (sygas).

2.2 THE TRULY RENEWABLE OPTION: SOLAR-TO-FUEL

Putting aside for a second the debate about which one is the best energy vector, now it’s clear that the main problem is the production process of the fuel in question. Both syngas and hydrogen are currently synthesized releasing vast quantities of carbon dioxide in the process.

So the great shift in technology is not the choice of the fuel but the process and in the resources used in its formation. Solar-to-fuel systems have been under way for a
number of years with one of the main objectives being the storage of the intermittent energy from the sun through the generation of a fuel. The key and the main advantages of this concept lies in the fact that a solar-to-fuel system uses the vastest, greenest and most abundant resource that we have with the most effective way that nature and science has designed to store energy: chemical bonds.

<table>
<thead>
<tr>
<th>Method</th>
<th>Energy Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compress air</td>
<td>0.512 MJ/kg, 0.16 MJ/L (at 300 bar, 12°C)</td>
</tr>
<tr>
<td>Pump water uphill</td>
<td>0.001 MJ/kg, 0.001 MJ/L (100 m dam height)</td>
</tr>
</tbody>
</table>
| Capacitors            | Ultracapacitors: 0.0206 (MJ/kg)  
                        | Supercapacitor: 0.01 (MJ/kg) |
| Batteries             | Li ion: 0.54-0.72 MJ/kg  
                        | NiCd: 0.14-0.22 MJ/kg  
                        | Pb: 0.14-0.17 MJ/kg |
| Chemical bonds        | Compressed H₂: 143 MJ/kg, 5.6 MJ/L (at 700 bar)  
                        | Liquid fuels 44(±4) MJ/kg, 38(±4) MJ/L |

Figure 10. Comparison between different energy density storage methods.

There is no argument, Nature is the proof, and the longevity of the fossil fuel economy is a confirmation: chemical bonds are in order of magnitude more efficient in storing energy than any other system ever designed, as is illustrated in Figure 10. Since solar-hydrogen system’s energy storage method has less energetic losses than common battery systems and hydrogen can be used either by internal combustion engine (ICE) or a fuel cell, solar-hydrogen system is currently considered the promising choice but solar
hydrogen systems do not directly attack the CO2 problem. So it can be considered an incomplete solution to our problem.

Of course if there was not an excess of CO2, the Solar-to-Hydrogen would have been the best choice but, right now, we have so many CO2 sources since our present energy-paradigm is based on burning fossil fuel that, as long we continue with this paradigm, we will always have an excess of CO2. That’s a problem that cannot stay unsolved. We are looking for a flexible solution that can switch from reducing CO2 to an eventual future hydrogen economy in a heartbeat using the sun as the only input.

2.2.1. Solar-to-Fuel production

The three main pathways to produce fuel with the aid of solar energy are:

- electrochemical;
- photochemical (or photobiological);
- thermochemical

Let’s consider, for now, hydrogen as a fuel for the solar-to-fuel production just to have an idea of how the different systems can work.
A solar-hydrogen electrochemical system generally is considered the process that using solar panels (photovoltaic PV system) supplies electric power to a hydrogen generator (electrolyzer) [14].

The coupling of these two sub-systems requires a number of conditions including:

- it should supply a minimum voltage to the electrolyzer for carrying out the splitting of water (theoretically 1.23V and experimentally around 1.45-2V)
- it should contain a minimum of auxiliary systems to increase global efficiency [14].
- it should work at its maximum power point (MPP) in order to realize a maximum global efficiency [14].

Even if electrolysis is a flexible process able to hit high efficiency and robustness both at high and low pH allowing a good electric-to-chemical energy conversion is not suitable for large scale renewable storage usage since commercial water splitting systems still have prohibitively expensive costs, even higher for non-concentrated solar energy-systems.

The photochemical-biological way / photocatalytic way: basically reproduces the electrochemical system with the addition of the uses some catalyst that allows the splitting of water at relatively low temperatures. These systems produce hydrogen directly from sunlight and water, offering the possibility to increase the efficiency of the solar-to-
fuel (hydrogen) production; in this way it’s possible to lower the cost of the system, but they still require surface-area to collect sunlight. (We have chosen this as the best approach and it will be discussed in depth in the final sections).

A **thermochemical system** is based on the concentration of solar radiation as energy provider to perform high-temperature reactions that produce hydrogen from water splitting.

These methods require “endothermic reactions that make use of concentrated solar radiation as their energy source of high temperature process heat” [14].

Thermal decomposition of water usually requires temperatures greater than 2,000 °C, which is a temperature achievable through solar thermal systems. [14].

From this analysis the best pathway for producing fuel with the aid of solar energy is the photocatalytic method since it lowers the energy input requirements, reduces costs, raises efficiency and still has a great room for improvement; plus is the closest to nature mechanism.
2.3 **ULTIMATE SOLUTION: Following Nature’s blueprint**

Considering the previous analysis we can say that what we need is a not an oil-linked way to easily store the sun’s energy in all large-scale-cheap way and capture and re-use CO2.

That’s exactly what has sustained the planet so far, that’s what each and every plant does and so this is what should be seen as the best example to follow in order to solve the energy and pollution problem at the same time. Nature gives us the exact blueprint of what we should do with photosynthesis.

We are looking for a way to store the sun’s Energy that must be not only CO2 emission free but also a way to absorb or reuse the CO2 currently produced from all the actual fossil fuel based sources of energy. It still has to be easily produced in a large-scale-cheap way, producible “in loco” and could make the transition to the hydrogen economy without big structural changes.

A renewable way to capture and reuse CO2 and store the sun’s energy into chemical bonds, all at the same time, without using any external input but the sunlight, seems the only connective link to pass from our current greenhouse-gas-era to a fully-renewable-era and it’s exactly what nature has been doing since the very beginning of life.

*How does photosynthesis store Energy by water splitting?*
The primary steps of natural photosynthesis involve the absorption of sunlight and its conversion into spatially separated electron/hole pairs. This separated electron/hole pairs built-in a wireless current where the holes are then captured by the oxygen-evolving complex (OEC) and used in the oxidation of water to oxygen while electrons, captured by photosystem I, reduce NADP+ (nicotinamide adenine di nucleotide phosphate) into NADPH (the reduced form of NADP+), nature’s form of hydrogen. Thus, the overall initial events of photosynthesis store solar energy in a fuel by rearranging the chemical bonds of water to form H2 (i.e., NADPH) and O2. [12].

Simplifying: light comes in, hits H2O and make H2 and O2 (NADPH) and then takes H2 and fixes it with CO2. The basic equation says:

\[ \text{Light} + H_2O + CO_2 \rightarrow O_2 + \text{Sugar} \]

But the CO2 part, the Calvin cycle, doesn't store energy so we don't need to replicate it. All of the energy storage process is in splitting H2O. But we cannot just take H2 and O2 from plants or just the energy they’ve stored because plants use almost all the energy to live and to be in their cells to stand up and they need to finish all the process, with the Calvin cycle, to do that.

Plants take in CO2 + H2O; H2O has low energy bonds (O-H), plants use sunlight to rearrange these bonds from O-H to H-H and O=O bonds which are high energy bonds. So they’ve made a fuel. Than with the Krebs cycle, adding CO2, in an energy free reaction,
they make sugar and they provide for their structural formation. So, when we eat the sugar taken from plants for our natural energy needs, we are just releasing the energy previously stored by the plants; so actually, every time we bite a green leaf or a vegetable, we are literally chewing photons from the sun.

   It is also worth underlining that we have a kind of natural fuel-cell in our body too; it is called cidocrum oxidotus; so we are really getting powered by the sunlight ourselves and that’s what our future should point to.

   So we have plants storing sunlight energy in these high energy bonds (HH, OO) which they then released and used later; and that’s exactly what we need to reproduce to solve our energy problems.

   Photosynthesis is taking H2O to O2 + (4H + 4é)( NADPH) and then H is attached to CO2 to make carbohydrates.

   When we eat carbohydrates what we actually do in our body right away is get the CO2 with the H2, breath the CO2 out and get the 4 protons + 4 elections back; then, inside our body we have a natural fuel cell called Cytochrome c Oxidase, an enzyme in our mitochondria, which takes the O2 that we breathe in plus the H2 from carbohydrates and make H2O and take the excess energy which actually powers us. So we’ve just taken light to rearrange bonds and store its energy and rearranging back to release that energy when the demands comes.
What I would like to do now is show how water split by sunlight makes H and O and then burns it in our house and powers our life just as we've been designed to do for ourselves.

_How much energy is stored in water splitting?_

Splitting 1 L of water we can store 13 MJ of energy. So making a simple approximation in an Olympic pool there are approximately 3.2 million L of H2O so if we convert globally a volume of water equal to the content of an Olympic pool to H and O per second we are able to store 43 TW. And remember, we don't use it up because when H and O recombines we get water back + the excess energy so we actually never use, never consume the water.

So to get this 16 TW we only need to convert globally per second one-third of the volume of the water contained in an Olympic pool. Now if we consider the average efficiency of a fuel cell (50%) we can conclude that just two-thirds of an Olympic swimming pool can store enough energy to power the World.

As is emphasized in the global energy calculation section the energy that the Sun reverses on the Earth every second provides more energy than our most pessimistic estimates; we only need a way to capture this energy and release it when we need it and the nature has shown us the best way.
To explain the “Why” and the “How” we have first to fully understand the answer to these questions:

*What is a fuel? What makes something a potential fuel?*

The capacity to efficiently store a large amount of energy in a small amount of space, in a safe and accessible way defines a fuel.

The most efficient and effective way that nature has engineered to store energy is in chemical bonds, and (as we have discussed earlier) that’s why a battery has no great room for improvement, it only needs to provide a small amount of energy.

Going back to the chemical bonds system of storing energy, take gasoline for an example: CC and CH bonds are high energy bonds: then you burn it with oxygen and they go to a lower energy bonds: CO and CO2 (OH H2O); so basically you take the high energy bonds convert them to low energy bonds and take out the excess energy and use it, that's how a fuel works.

### 2.3.1 Collecting Sun energy: Photosynthetic vs Photovoltaic Efficiencies

In order to design a new solar-to-fuel system we have to go back to the main initial phases of natural photosynthesis which include the absorption of sunlight and its
conversion into spatially separated electron/hole pairs and compare it with our capacity to collect sunlight.

Beginning from efficiency, which can be considered a fairly simple and univocal concept in engineering, it can become elusive and complicated even to define when the systems to evaluate or to compared to are such as living organisms.

Starting from a PV device, the solar conversion efficiency is generally defined as the ratio between electrical power out (W/cm²) divided by incident solar irradiance (W/cm²) measured over the entire solar spectrum and so it can be easily and accurately measured[13].

But using the same classical approach just described to natural photosynthesis we will exclude other important parameters that in some cases are essential for making it so effective and efficient especially in terms of energy storage and transmission. In fact, natural photosynthesis tend to use much of this stored energy, collected in the chemical bonds of its molecular products, to sustain and replicate the organism and do not accumulate much more extra storage.

So a more fair and direct comparison of PV and the natural photosynthetic solar energy conversion efficiencies would be analyzing a process in which both, PV and natural photosynthesis, stores energy in chemical bonds.
Finding this commune path is the real challenge, here is the key that moved our research focus: finding the best way to store through the PV technology the solar energy into chemical bonds and it will be further developed in the following chapters while in this one we limit to make a fair comparison between nature and the current possibility commercially available following as it-s already been investigate in Science’s publication “Comparing Photosynthetic and Photovoltaic efficiency and recognize the potential for improvement” [13].

Since the process in which PV also stores energy in chemical bonds is needed in order to make a fair comparison and considering that nowadays the main applications of PV-derived energy is the electrolysis of water, we are going to use this system, the electrochemical for this analysis. Basing our discussion on existing commercial electrolyzes we can use for the artificial side their accurate efficiency benchmarks where the key element is the free energy needed in order to split H2O into H2 and O2 (DG° = 1.23 eV) that it can be essentially associated to the free energy change in photosynthesis [DG° = 1.24 eV for CO2 + H2O to (CH2O) + O2, where (CH2O) is shorthand for carbohydrate].

The power conversion efficiency, previously defined, for the currently commercialized single-junction (single photosystem) silicon solar cell modules is generally 18% under standard conditions such as 1 Sun solar intensity (1 kW/m2), with an AM1.5 spectral distribution or solar zenith angle of 48.2° (sunlight passing through 1.5
atmospheres) [13]. But to have a proper point of view we have also to consider that the efficiency of a PV module varies during the day and throughout the year because of the changing solar zenith angle so we can fairly assert that the PV efficiency is lower than the one previously stated, is about 95% of the maximum AM1.5 value [13].

Considering now the storage process we investigate the electrolyzers which have quite high efficiencies, about 80% [based on heat of combustion of H2 to H2O in liquid form at atmospheric pressure and 25°C, standard temperature and pressure (STP) conditions]. So coupling this two system, assuming that there is no mismatch between the photovoltage generated by the PV array and the voltage required for electrolysis, we can estimate the yearly averaged efficiency for Sun’s powered water splitting by PV-driven electrolysis \([(0.18)*(0.95)*(0.8)] \sim 14\%\). To be completely fair in general Si PV modules suffer mismatch losses as high as 20 to 30%, since their electrical arrangement in series, this would so lower the overall H2O splitting efficiency down to \sim 10 to 11\% [13]. This first analysis could be chosen as the starting point for comparing it with the efficiency of artificial photosynthetic fuel production.

On the other hand in order to best describe natural photosynthesis several different measures of efficiency have been used for instance quantum efficiency is one of them, it is the percentage of absorbed photons that give rise to stable photoproducts. In fact under optimum conditions bio-photosynthetic organisms normally operate at nearly 100% quantum efficiency [13].
One of the best parameters to get a clear perception in the comparison between the energy efficiency of photosynthesis and PV electrolysis over an annual cycle, is defined as the ratio between the energy content (heat produced by the combustion of glucose to CO2 and liquid H2O at STP) of the biomass harvested annually from a certain surface and the annual solar irradiance over that surface [13].

According to this assumption solar energy conversion efficiencies for crop plants do not exceed 1% in both temperate and tropical zones. This value do not nearly reach the benchmark for PV-driven electrolysis [13].

Furthermore, a thermodynamic analysis shows that in natural photosynthesis not all the energy in each absorbed photon can be captured for productive use.

Considering a realistic photoelectrolysis cell, structured with a single-threshold semiconductor photoelectrode (in direct contact with water) that generates hydrogen and oxygen at finite rates, it has to be expected that the overvoltage would be finite.

So it can be concluded that further improvements in productivity for both photosynthetic and PV systems can be reached by resetting the limits to energy conversion through a newly designed system [13]; an idea that will be discussed in Chapter 3.
In fact according to Professor Blankenship “there is clearly a need to apply both in the service of sustainable energy conversion for the future” [13]. This means focusing on technologies in which photovoltaics are coupled to redox in photo-electrochemical cells or even considering the use of living organisms for solar fuels production. He continues by saying that numerous points inefficiency of the natural system can be subjected to “improvement by using genetic engineering and more aggressive techniques of synthetic biology” [13].
CHAPTER 3

CONVERTING SUNLIGHT INTO A DIFFERENCE OF POTENTIAL

At this point the aims and requirements of this research are clear so it is time to discuss how this new system can become possible. One major step is efficiently collecting sun energy. As discussed in the previous chapter the PV, which is the current way to collect the Sun’s energy, is one of the major areas of improvement in creating an efficient solar-to-fuel conversion.

In this chapter how this improvement can be achieved and which technologies have to be adopted will be discussed. The use of p-i-n structured semiconductor with the major focus on amorphous Si pin photodiode will be introduced and discussed. With this technology a potential difference between the two semiconductor’ sides when exposed to light can be generated. The chapter will be concluded with the description of a triple junction a-Si structure which is our final choice to collect the sun’s energy and so produce the potential needed to perform the reactions needed to store the sun’s energy.

3.0 Initial Reflection

Comparing natural (photosynthetic systems) and artificial (photovoltaic) solar Energy storage systems, narrowing the analysis to the power point of view it can be asserted that the efficiency advantage clearly goes to the photovoltaic systems.
As previously stated according to Professor Blankenship “there is clearly a need to apply both in the service of sustainable energy conversion for the future” and so focus on technologies in which photovoltaics are coupled to redox in photoelectrochemical [13].

3.1 **AMORPHOUS SILICON**

The atom of silicon tends to form four covalent bonds with the neighboring atoms symmetrically organized in a “tetrahedral” configuration, perfectly maintained in the “diamond” lattice of crystal silicon. In crystalline silicon (c-Si) this tetrahedral structure continues over a large range while in amorphous silicon (a-Si) this long range order is not present. In a-Si the continuous random network of atoms sometimes have dangling bonds. This type of defect causes anomalous electrical behavior.

As all semiconductors do, a-Si absorbs those photons from an incident light beam that have photon energies exceeding some threshold energy. These photons once absorbed generate positively charged “holes” and a negatively charged electrons.

Solar cells require that photo-generated electrons and holes have to be separated by relatively modest electric fields that are “built-in” to the device, and amorphous silicon and many other non-crystalline semiconductors are unsuitable in the production of efficient cells. A solution to this issue is in the pin structure achieved by doping crystal Silicon:
• Phosphorus doping: induces a conductivity associated with mobile electrons (the material was “n-type”) increase of mobile electron.

• Boron doping: induces a conductivity associated with mobile holes (the material was “p-type”). Increase in the number of holes.

During the evolution of this technology and once the knowledge on this material has become more secure, it has emerged that during then plasma-deposition of amorphous silicon a significant percentage of hydrogen atoms bonded into the amorphous silicon structure giving to the material certain characteristics essential to the improvement of the electronic properties. In fact the material can be passified by hydrogen, which bonds to the dangling bonds. This improved form of amorphous silicon has generally been known as hydrogenated amorphous silicon (a-Si:H) but recently the term amorphous silicon has been used to refer to the same hydrogenated form (the unhydrogenated forms of amorphous silicon are only infrequently studied today). Hydrogenated amorphous silicon (a-Si:H) has a sufficiently low amount of defects to be used within devices such as solar photovoltaics cells (PV) [7].
3.2 **PIN PHOTODIODES**

The fundamental unit that constitute a photoactive amorphous silicon-solar-cell is a photodiode: a three layers structure deposited in either the p-i-n or the n-i-p sequence.

The usual thickness of these layers are: 20 nm for the p-type, a few hundred nanometer for the undoped-intrinsic (i) layer, and a very thin n-type layer. As explained in Figure 11, the excess of electrons produced in n-type layer are donated to the p-type layer, leaving the layers positively and negatively charged (respectively); in this way a sizable “built-in” electric field (usually more than 104 V/cm) is formed [7].

![PIN Photodiode Diagram](image)

Figure 11. a-Si p-i-n structure.

When sunlight hits the photodiode, a stream of photons that pass through the p-type layer, which is a nearly transparent layer so called “window” layer, so solar photons are mostly absorbed in the much thicker intrinsic layer.
Each photon that is absorbed will generate one electron and one hole photocarrier. The photocarriers are swept away by the built-in electric field to the n-type and p-type layers, respectively thus generating solar electricity [7].

The importance of the thicker undoped-intrinsic middle layer is due to the fact that in doped a-Si:H minority photocarriers (holes for n-type, electrons for p-type) do not move very far this implies that a simple p-n structure would too few photocarriers collected only from photons generated in the extremely thin layer of doped a-Si:H. [7].

Plus, in analyzing the performance of a-Si:H-based solar cells, one normally considers any photons absorbed by the doped layers to be “wasted.”

In order to capture most of the sunlight the best solution is to keep the doping atoms out of the absorber layer enabling this middle un-doped layer to be thick enough.

### 3.3 MULTIJUNCTION SOLAR CELLS

Another further improvement to direct conversion of sun energy in built in potential in amorphous silicon can be found in the fact that Silicon solar cells can be stacked creating a structure called multijunction solar cells.
This structure can be easily achieved especially in amorphous materials, both because there is no need for lattice matching, in fact it requires crystalline heterojunctions, and also because the band gap is readily adjusted by alloying.

![Diagram of multijunction a-Si structure](image)

Figure 12. Multijunction a-Si structure [7].

Figure 12 illustrates the layout of two junctions (two p-i-n photodiodes) in series: a tandem cell. So the conversion efficiency of the single-simple structure of the a-silicon single-junction pin photodiode can be strongly improved by creating a “multijunction” device with the superposition of two or three such photodiodes, one on top of another. We illustrate a “tandem” device which shows a combination of two pin diodes in which the “bottom” cell is amorphous silicon germanium alloy [7].

This detail has not to be left out because the a-SiGe:H is fundamental in the “spectrum splitting” of the solar illumination, essential feature of Multijunction structure.
Made by including germane (GeH4) gas in the plasma-deposition, a-SiGe:H contributes to the main advantage of the tandem design over the simpler single-junction: “spectrum splitting”. “Spectrum splitting” of the solar illumination that is essential in improving the efficiency since the absorption coefficient of light rises rapidly with the photon energy causing the topmost layer of a tandem cell to act as a “low-pass” optical filter.

So the “spectrum-splitting” effect is the phenomenon consequent to the deposition of a second pin junction structure on top of a first one. This top junction “filters” the sunlight removing from the light that reaches the bottom cell the photons absorbed in the top junction [7].

But this is not the only advantage. In fact we distinguish three main reasons that justify the improved efficiency in a-Si-based multijunction cells over single-junction cells:

- The spectrum-splitting effect we have just described.
- The i-layers in an optimized thickness: multijunction cells are thinner than in singlejunction cells as can be seen in the Figure, this “junction thinning” is required because each individual junction has to have a better fill factor than the singlejunction device so will also be less variation in efficiency from the initial to the stable one.
• Higher operating voltage and lower operating current: multijunction cells produce their power at a higher operating voltage and lower operating current than a single-junction cell; this effect on the current will reduce resistive losses as the current flows away from the junctions and into its load.

In conclusion, the upside of the multijunction design are strong enough to overcome the additional complexity and cost of the deposition facility.

3.3.1 a-Si/a-SiGe/a-SiGe TRIPLE-JUNCTION SOLAR CELL

A reengineering of the use of the a-Si photovoltaics pin junction has conducted the industry to the creation of several types of multijunction solar cells. From the cost point of view dualjunction a-Si/a-Si (same band gap tandem) solar-cells have minor production costs compared to tandem cells doped with Ge (a-SiGe) but this causes a reduced efficiency compared to more advanced triplejunction production path [7].

So higher conversion efficiencies is achieved from dual-junction a-Si/a-SiGe cell and triple-junction a-Si/a-SiGe/a-SiGe cells thanks to the spectrum-splitting analysis which permit a higher collection of the sunlight.
Giving just a little bit more details of the structure used in the set-up described in chapter 6 purchased from the company Xunlight: a-Si(1.8 eV)/a-SiGe(1.6 eV)/a-SiGe(1.4 eV) triple-junction solar cells have been used to obtain the most efficient a-Si-based cells today [7].

![Structure of triple-junction nip substrate-type solar cells](image)

**Figure 13.** Structure of triple-junction nip substrate-type solar cells [7].

Figure 13 shows the structure of a triple-junction substrate cell grown on stainless steel foil. In both triple and double-junction, light enters from the p-layer this implies that holes need to travel a minor distance to get collected compared to electrons. In the deposition process of the nip cells on an SS substrate the first step consists in the deposition
of a reflective metal layer on the substrate by sputtering or evaporation, followed by the sputter deposition of a ZnO buffer layer [7]. As reflective layer either silver (for research) or aluminum (for production) is usually used because of their high reflectivity.

The deposition of the metal layer occurs at a temperature between 300 and 400 Celsius. The first deposited is the bottom nip with an a-SiGe i-layer (1.4–1.5 eV band gap) to which is added a second a-SiGe-based middle cell (1.6–1.65 eV i-layer band gap) and so the top a-Si-based cell (1.8–1.85 eV i-layer band gap) is added as last. It’s important to underline that the intrinsic layer is made by using high H dilution at relatively low temperature.

A further layer of indium-tin-oxide (ITO) of approximately 70-nm is deposited on top of the a-Si-3jn via evaporation or sputtering; it serves both as the top electrode and an antireflection coating.
3.3.2 **Current matching**

As has just been explained, in a triple-junction cell the three single-junction cells are monolithically stacked on top of one another in order to create a unique two-terminal device. To achieve this synergic structure these component cells are connected in series but because of this the cell with minimum current density during operation will limit the total current of the triple-junction stack. So it’s necessary to match each and every current densities of the component of the cells at the maximum power point in sunlight.

The short-circuit currents JSC of the component cells can be adopted as a rough starting base to this matching. Considering our a-Si/a-SiGe/a-SiGe triple-junction cell, the bottom a-SiGe cell usually has the lowest FF and the top a-Si cell usually has the highest FF which means that the JSC of the bottom cell needs to be slightly greater than the JSC of the middle cell, which in turn needs to be slightly greater than the JSC of the top cell [7].

It’s also important to underline that these current matching adjustments also have other benefits; in fact the bottom cell benefits from the light enhancement from the back reflector (see Figure 13) while the middle and top cells receive little benefit from the back reflector.
3.3.3 **Tunnel junctions**

The interfaces between adjacent pin cells are another step that needs attention in the fabrication of a multijunction solar cell and these are called tunnel junctions. These interfaces which lie between n-type and p-type layers do not only have the electrical properties of a classic p-n junction diodes; in fact it one other important fact has been proved. The direct consequence of an increase doping is the formation of dangling bonds [7]. This means that carriers that are “trapped on defects on one side of the interface can move to traps on the other side simply by quantum mechanical tunneling” [7]. In a mechanism sufficiently efficient to “short-circuits” electrical transport involving the conduction band and valence band states [7].

This means that the doped layers at the tunnel junction are made with very high doping, particularly the sub-layers near the interface; in this way the efficient recombination (by tunneling) of holes from the cell below and electrons from the cell above is permitted by the large density of dangling bonds, as illustrated in Figure 16. This tunnel junction is reverse biased under normal operation; In order for the system to work this tunnel junction must generate negligible VOC, have negligible resistance and optical absorption too [7].
3.3.4 I-V measurement

In the process of understanding and monitoring the I–V performance of a multiple-junction, spectrum-splitting solar cell, we will mainly focus on the spectrum of the illuminating light.

Before starting the analysis it’s important to premise that for a triple-junction cell, for which the p-i-n component cells are currently-matched under the standard AM1.5 global spectrum, we can find a poorer performance under a different light source (example tungsten lamp).

About the short circuit current density (JSC), the triple-cell usually has a JSC close to the JSC of the limiting component of the cell except when there is a large mismatch and the limiting cell has a very low fill factor (FF).

About the open circuit difference of potential/overpotential (VOC) of the triple cell, it is the sum of the VOC of the cell’s component (and reduced by any photovoltages at the tunnel junctions). It’s also important to underline that the properties are not equally distributed in a triplestack cell [7].

In fact the bottom component of the cell generates just about the 33% of the photocurrent that would be produced under full sunlight and its VOC is a little bit smaller (usually by 20 mV) than when it’s fully exposed to sunlight; while the middle cell will
have around 50% of the current that would be produced with the full exposition. Another property that directly depends on the limiting component of the cell and on the current mismatch among the cell’s components is the fill factor. A large mismatch leads to a higher triple-cell FF but, on the other hand, it also leads to a lower triple-cell current, so in order to have the best performance in the cell the proper equilibrium has to be found [7].

3.3.5 Quantum efficiency measurements in multijunction cells

In order to properly measure the QE of a triple-junction solar cell the appropriate light bias and electrical bias needs to be applied. Without these optical and electrical biases a direct QE measurement of one single junction cell is the only possibility, which would yield a “delta”-shaped curve, because in order to allow the current to flow through the cell all of the component cells are illuminated simultaneously.

In order to measure the QE of a specific component cell, say the middle cell, only the top and bottom cells should be illuminated, so a DC bias light is illuminated on the cell through a filter that transmits only blue light and red light so that the top and bottom cells are illuminated.

This condition limits the middle cell current flow when the light through the monochromator is absorbed by the cell. This means that the
current through the sample is that of the middle cell, that is, the AC photo current at the monochromatic light that is absorbed in the middle. Quantum efficiency curves of component cells of a typical triple-junction solar cell. The table indicates the short-circuit current densities JSC for the component cells measured for AM1.5 illumination and with a xenon illuminator cell [7].

Furthermore, thanks to the fact that this AC photocurrent is modulated by an optical chopper, it can be easily detected using a lock-in amplifier.

The same procedure, with the exemption of different optical filters for the bias light need to be used, can be adopted to monitor the other two component cells.

Another important fact is highlighted while testing the cells without externally applied electrical voltage bias: it can be observed that the component cell tested is actually under reverse bias, given by the total of the VOC registered from the other two component.

In this case, when the measurement is made without externally applied electrical voltage bias, the QE curve indicates the QE of the cell under reverse bias condition, which can be approximatively associated with the QE under short-circuit condition when the component cell FF is high [7].

But to actually measure the QE under short-circuit current condition, the required
electrical voltage has to be externally applied in order to cancel out the voltage generated by the other component cells under the optical bias light.
CHAPTER 4

OXYGEN EVOLUTION REACTION

As anticipated in the preliminary summary the core of this work comes from two research projects: the water splitting performed by Professor Nocera’s research group and the CO2 reduction performed by Professor Salehi’s group.

In this chapter the water splitting mechanism will be discussed and in particular the Co-OEC (Oxygen Evolving Complex) which is one of the ingredients of our final idea. The oxygen Evolution Reaction, in fact, covers one of the two semi-reactions that are required to happen in the final set-up (Chapter 6). In this chapter an explanation will be given regarding this catalytic mechanism, on the catalyst formation and properties, with a major focus on its self-repair mechanism, and on the different system to which this catalyst can be coupled: direct and indirect water splitting. Finally the efficiency of these systems will be discussed including the parameters to take into account.
4.1 **THE CATALYST: Co-OER**

In the photosynthesis process electron/hole pairs get separated from the sunlight input so in order to duplicate this artificially a photosynthetic membrane has to convert sunlight into spatially separated electron/hole pairs within a photovoltaic cell and then capture the charges with catalysts that mediate “water splitting”

Chapter 3 explained how to achieve this conversion of sunlight into separated electron holes pair though an a-Si-3jn, now let’s focus on how our four holes are captured by a catalyst at the anode to produce oxygen, and how the four electrons are captured by a separate catalyst at the cathode to produce hydrogen or, as will be discussed in Chapter 5, reduce CO2 to CO. The net result is the storage of solar energy in the chemical bonds of O2 and, in this case, H2.

Since the OER catalyst, that will be used in the final set-up, is first designed for water splitting, to have a better perspective of his characteristics and catalytic mechanism, it will be now analyzed in the water-spitting mechanism. So, let’s theoretically inquire the efficiency of a water-splitting catalysts which is the determining factor for energy storage in artificial photosynthesis.
Starting from the fact that the additional voltage to E (Nernstian potentials) that is required to attain a given catalytic activity (overpotential) limits the efficiency of converting light into catalytic current. Of the three reactions, HER, OER and CO2 reduction, the OER (H2O → O2) is considerably more complex and requires more overpotential.

The OER requires it’s a four-electron-oxidation process involving two water molecules from whom are removed the four-protons of the relatively weak-bond O=O.

For a classical electrochemical cell, usually, another important characteristic is required for the catalyst in order to control this proton-coupled electron transfer (PCET): having a high and enduring tolerance to oxidizing conditions especially considering that even at the thermodynamic limit, OER requires an oxidizing power that causes most chemical functional groups to degrade.

But, if the requested environmental conditions are not that extreme, this issue disappears[12].
Another aspect that can be determinant is in the ambient condition using a catalyst that efficiently operates in neutral water: few catalysts are efficient in a neutral environment. Usually neutral water is oxidized at Pt electrodes and other precious metal oxides have been reported to operate electrocatalytically in neutral or weakly acidic solutions [20]. So the real challenge now is the development of an earth-abundant, first-row catalyst that operates at pH 7 at a low over-potential.

So, inspired from the Photosystem II, trying to keep the electrical properties of the expensive commonly used catalyst, such as Pt, the MIT group has synthesized a catalyst that is earth abundant and highly manufacturable called Co-OEC.

The operating condition for oxygen generation to occur doesn’t require any extra effort: the benign conditions are pH = 7, 1 atm, and room temperature.

Cobalt ions in the presence of chemical oxidants such as Ru(bpy)3 3+ (bpy, bipyridine; Eo = 1.26, where Eo is the standard potential) catalyze the oxidation of water to O2 in neutral phosphate solutions [27, 28]. Oxygen yields drop in these reactions when oxidized Co species precipitate from solution because the catalytically active species is removed from the solution-phase reaction. [12].

During the catalyst formation it’s noticeable a dark coating forming on the ITO surface and effervescence from this coating vigorously increase. Similar results are reported with other cobalt compound like the Co2+ source, which underlines that the original Co2+
counterion is unimportant and so it’s relevant to assert that this activity does not depend on an impurity found in a specific source [12].

During the course of an 8-hour electrolysis it’s so reported that the amount of charge passed far exceeds what could be accounted for by stoichiometric oxidation of the Co2+ in solution behavior indicative of the in situ formation of an oxygen-evolving-catalyst as reported in the cited publication [12].

These results herein highlight a new area of exploration for the development of easily prepared, earth-abundant catalysts that oxidize water. Furthermore the catalyst reported here has many elements of natural photosynthesis, including:

(i) Formation from earth-abundant metal ions in aqueous solution[12].

(ii) Possible pathway for self-repair[12].

(iii) Carrier for protons in neutral water[12].

(iv) Generation of O2 at low over-potential, neutral pH, 1 atm, and room temperature [12].

The molecular cubical catalyst of photosynthesis almost perfectly overlaps the catalyst used in this reaction. These structures are very close but the one synthetized by Nocera has cobalt instead of manganese. This Co-OEC forms spontaneously in the glass of water as soon as the electricity turns on: the cube forms and then it starts splitting water
to O2 and, exactly like what it happens in photosynthesis, it decomposes itself. The cube falls apart while it's operating but the phosphate actually drives it back and reassembles it[12]. And so it's called self-healing: it's always fixing itself.

**4.2 SELF-REPAIR MECHANISM**

Jim Barber, Professor of Biology at Imperial College, has figured out in the last few years exactly what plants look like inside. This complex network allows the plant to operate in different conditions [3].

The other thing it has been noticed with these plants is that when you spilt water to oxygen and hydrogen it's so vicious that it starts heating the plant until it dies; so, every 30 minutes, the plant takes this big protein and removes it, this coaster falls apart so that the plant can damage itself and then rebuild itself and refresh and fix itself [3].

That's the opposite of how science generally works: scientists try to make things really stable forever. Letting it be unstable, which basically means not expecting a constant output, is exactly how Nature works and exactly what can makes this system dynamic and suitable in a large number of different condition without any external re-setting. So, based on this observation, we should decide that also the photosynthetic community has to let it be unstable and just try to fix it [3].
Considering the Co-OEC just described in situ formation, described in the previous paragraph, also implies a self-repair mechanism. This molecular mechanism involving O2/H2O is cyclical and it happens in Co centers suggesting that catalytic reactions cycles among Co2+, Co3+, and Co4+ oxo oxidation states.

This means that if a catalytic cycle involves an oxidation state that is prone to dissolution, this process can be countered by continual catalyst formation by establishing an equilibrium with the judicious choice of an anion.

The main basic advantages of this self-healing function are:

- It is a third as cheap
- It works in inexpensive environmental conditions
- It's highly manufacturable

In fact the most effective and common catalyst so far has been platinum but since we are operating in a neutral environment (water) the platinum is no longer necessary. With cheap metals, cheap cobalt catalyst, cheap substrates (it's even better than Pt) a structure has been obtained that looks like the cube of photosynthesis and also behave in the same way:

And because it's always fixing itself you can use it in salt water, river water and human waste water (front and back) and all of this because nothing can deteriorate it because as things start to fail it's breaking down and it’s healing itself, always giving “a fresh face”.
Monitoring over the course of the electrolysis, the behavior changes: the over-potential required to operate the Ni electrode at 1 mA/cm² current density increases from 540 to 620 mV in Charles River and from 570 to 650 mV in seawater, while, on the opposite, it is observed for Co-OEC in 1 M KBi, prepared using Charles River and seawaters, only a modest increase in electrode over-potential after 4 h of electrolysis (460 to 480 mV and 530 to 550 mV, respectively) as reported by prof. Nocera [3-5].

4.3 CATALYTIC CONCLUSION

The reactions occurring in the reactor (as in most of the reactors of this type) are reduction-oxidation (redox) reactions. In general, in the oxidation step (at the anode) electrons are released due to the oxidation of a chemical species. The electrons are sent to an external load and, through it, flow toward the cathode. At the cathode a chemical species is reduced, acquiring the electrons coming from the eternal load. The full redox reaction can be therefore divided into two half-cell references that develop in physically separate regions of the reactor. The electrolyte interconnects the two regions (cathode and anode) providing the conductions of ions.

The results led us to conclude that the Co-OEC is the result of the development of an easily prepared, earth-abundant catalysts that oxidize water which has the potential to
enable the storage of solar energy in an order of magnitude commensurate with global demand.

In situ formation also implies a self-repair mechanism which means that if a catalytic cycle involves an oxidation state that is prone to dissolution, this process can be countered by continual catalyst formation which has as a consequence a process that is a third as cheap, it works in inexpensive environmental conditions and it’s highly manufacturable.

The description of electrodes functionalized with the catalyst’s performance is quantified by water-oxidation current density at fixed over potential and from the studies of doctors Esswein and Nocera it has demonstrated exceptional operational stabilities simply due to the increasing number of Co active sites [5]. Additionally, the fact that it operates at neutral with a near to neutral pHs contributes to “reduce the formation of passivating oxide layers of indigenous metals commonly found in natural water supplies (e.g., Ca(OH)2, Mg(OH)2, etc.)” [5] and inhibits denaturation of biomolecules, processes that, in caustic alkali, usually leads to electrode deactivation.

Now, since artificial photosynthesis has the potential to enable the storage of solar energy, the main point of this Chapter is to establish if its rate of storage is commensurate to global demand and the catalyst system just introduced seems to give to water-splitting chemistry the right pattern to be performed at a daunting scale.
These water-splitting catalysts comprising earth-abundant materials can be integrated with amorphous silicon with minimal engineering to enable direct solar-to-fuels conversion based on water splitting. The choice of the previously described cobalt catalyst, Co-OEC as the O2- evolving catalyst, enables the design of a completely new solar to fuel production system that can operate in neutral buffered electrolyte with pure or natural water at room temperature.

4.4 Co-OEC Solar Water Splitting: Indirect vs Direct Solar To Fuel

In the future era, according to what we will need to avoid, trying to follow what nature has taught us, there are two types of system that could answer the requirements previously addressed:

• Indirect Solar to Fuel (ISF)
• Direct Solar to Fuel (DSF)

Co-OEC catalytic solar water-splitting system: Preliminary Conclusions

In this section the development of solar water-splitting cells is described comprising earthabundant elements that operate in near-neutral pH conditions, both with and without connecting wires. The system consists of a triple junction, amorphous silicon photovoltaic interfaced to hydrogen- and oxygen-evolving catalysts made from an alloy of earth-abundant metals and a cobalt|borate catalyst, respectively.
The devices that will be described reach efficiencies of about 4.7% for a wired configuration and about 2.5% for a wireless configuration for the solar-driven water-splitting reaction, when illuminated with 1 sun (100 milliwatts per square centimeter) of air mass 1.5 simulated sunlight.

Exactly like in nature, fuel-forming catalysts interfaced with light-harvesting semiconductors afford a pathway to direct solar-to-fuels conversion that mimics many of the basic functional elements of a leaf [1].

The shifting concept respect the past here is that solar photovoltaic (PV) cells, which are normally used to generate electricity, here are used to directly generate fuels such as hydrogen from water or syngas from CO2 (as will be discussed in chapter 5 and 6) thus providing a storage mechanism for sunlight.

This type of scheme mimics the photosynthetic evolution inside a leaf that converts the energy of sunlight into chemical energy by splitting water to produce O2 and hydrogen equivalents or fixing CO2 to produce NADPH. In fact, one of the initial phases of natural photosynthesis involves the absorption-storage of sunlight and its conversion into spatially separated electronhole-pairs where the holes of this wireless current are captured by the oxygen-evolving-complex (OEC) of Photosystem II (PSII) to split H2O into O2 while electrons and protons produced as the by-products of the OEC reaction get transferred to
Photosystem I (PSI) to produce a reduced form of hydrogen in the form of NADPH (the reduced form of nicotinamide adenine dinucleotide phosphate) [1].

If we look carefully this process could be the perfect blueprint to create a totally new renewable and emission free way to store sunlight energy. Plus, it’s important to notice that the separation of light collection/conversion from catalysis is compulsory to the photosynthetic function because electron/hole pairs are generated one at a time and the water splitting reaction is a four electron-hole process. Both processes have to happen simultaneously and one counterbalances the other. And, since the light collection and conversion apparatus of the leaf is a four electron-hole chemistry, multi electron catalysts of PSII and PSI are needed to bridge the light-driven one electron-hole “wireless current”. [1].

The first step to mimic photosynthesis could be summarized in design a way to generate O2 and H2 with inorganic materials using fuel-forming catalysts interfaced with light-harvesting semiconductors.

A system of this type must generate electrons and holes with enough energy to overcome both the energetic barrier of water oxidation (1.23 V at standard conditions) or CO2 reduction (0.9 V) and any over-potentials needed to drive catalysis and it seems that using a a-Si-3jn (as described in Ch 3) is the solution to photo-produce enough potential.
But another practical problem remains; expensive catalysts and the harsh environment. Usually solar photochemical production of H2 and O2 from water at reasonable efficiency have relied on the “use of prohibitively expensive light-absorbing materials [e.g., (Al)GaAs and GaInP], and/or fuel-forming catalysts (e.g., Pt, RuO2, IrO2), and strongly acidic or basic reaction media, which are corrosive and expensive to manage over the large areas required for light harvesting”.

This type of problems seems to be solved by the adoption of the system described in the previous paragraphs because of its focus mimicking photosynthesis with materials composed of earth-abundant elements and with electrolytes near neutral pH conditions.

The success of this approach will enable novel PEC and other light-harvesting (e.g., wireless) architectures to be engineered to produce solar fuel at more practical cost targets.

The choice of the semiconductor is dictated by the same criteria: Silicon choice for constructing an artificial leaf is in fact dictated also from its earth-abundance and prevalence in the electronics and PV industries and the tunneling junction, explained in chapter 3, have also been explored enough guaranteeing the series rearrangement of different junctions. These solutions can be used in two different configurations: wired and wireless but the first one limits the application of Si in photochemical water splitting to a traditional, wired PEC panel geometry, which has traditionally proved too costly for commercialization.
4.4.1 **Indirect Solar to Fuel (ISF)**

This electrochemical system, already introduced previously in paragraph 2.2.1, will now be considered coupled with the catalyst system already discussed. In this way efficiencies never reached before in a solar-to-fuel system will be achieved.

![Diagram of indirect Solar-to-fuel device scheme and house set-up](image)

Figure 14. indirect Solar-to-fuel device scheme and house set-up

A device-system of this type (Fig 14) should include: PVC piping, cheap alloy, simple hydrocarbon separator as the catalyst; costs, for a prototype production, would only be about $30. The conversion performance of this system is just 10 time slower then a commercial (>1000$) electrolyzer; so the convenience of cost production kills the
electrolyzer supremacy. Plus this prototype works with every type of water while the electrolyzer only with the pure one and with a series of conditions that are not remotely as flexible as the one of this new system.

So the direct consequence of this project in the future will be a world off the grid: we will use PV during the day to run our houses and take a little bit of electricity to feel that the Nocera's device makes a H and O put them in tanks and then, when it's needed, feed it to a fuel cell, get current out and so power our houses at night, recharge the battery of our electric car or take directly the H and put it in a tank inside the car and run a fuel cell car or an internal combustion engine car.

*How much PV do we need to run this system?*

An average home requires 31.2 kW hour a day; the average output of PV: 5x6 = 30m^2 of PV = 6000000 mA with a 20 mA/cm^2 current density; that means that I just have to be able to sustain my reaction with a current density of around this 20 mA/cm^2 and so I don’t need to be at 1000 mA/cm^2 like for the classical electrolyzer system. So in less then 3.5 hours with a PV 6.5 m^2 on a rooftop enough water can be processed to store energy for two days, also because during most of the day I will be using PV directly so I will probably just need to take half of that spilt water [39].
4.4.2 **Direct Solar to Fuel (DSF): The ARTIFICIAL LEAF**

This system is the direct evolution of the indirect electrochemical system already explained in the previous paragraph. It is based on the same concept that will be used in the final design of this work: the direct, wireless conversion of the Sun into fuel. In the final design proposed in chapter 6 the oxygen evolution half of this cell is basically used to drive one of the two semi-reactions necessary to reconvert CO2 into fuel using just the input from the sun. So, for the rest of this paragraph, this set-up performing water-splitting instead of CO2 reduction will be explored just because the certified data are for this reaction but, the OER mechanism, is the same that will be used for the direct Solar-to-fuel CO2 reaction.


![Figure 15. Direct water splitting device scheme](image-url)
The system consists of a triple junction, amorphous silicon photovoltaic interfaced to hydrogen-evolving catalysts on one side and oxygen-evolving catalysts on the other both made from an alloy of earth-abundant metals and a cobalt| borate catalyst, respectively. The main difference between the indirect and the direct is in the complete absence of wires. This is a stand-alone device which is the closest to the natural leaf that we can get so far. It reproduces the wireless current between cathodic and anodic side exactly like what happens in the leaf and that’s the reason why this system is called “the artificial leaf.”

4.4.3 Direct Solar to Fuel panel Efficiency calculation

The condition that it has been considered for the efficiency calculation is the stand-alone operation of the cell with no external applied potential from an electrical power source (i.e., unassisted). The catalyst used is the Co-OEC coupled with 3jn-a-Si photoanode in conjunction with the NiMoZn cathode for H2 production [1].

In Nocera’s research the cathode catalyst is NiMoZn while in the set-up described in chapter 6 the catalyst used is MoS2, although in this section this different catalyst won’t be taken into consideration since it is not the one under examination.

The cell device was illuminated with AM 1.5 solar simulated light.
The solar-to-fuels efficiency (SFE) for conversion of light and water into H2 and O2 responds to this equation

\[
\text{SFE(\%)} = j \cdot \Delta E / S \cdot 100\% = J (\text{mA/cm}^2) \cdot 1.23 \text{ V/100 (mW/cm}^2) \cdot 100\% \quad (1)
\]

- \(j\) is the current density at the photo electrode
- \(\Delta E\) is the stored energy of the water splitting reaction
- \(S\) is the total incident solar irradiance, which is provided by the AM1.5 light source at 100 mW/cm².

(Figure 16A plots the efficiency and stability of Co-OEC | 3jn-a-Si | NiMoZn PEC cells operated in 1 M KBi (black trace) and 0.1M KOH (red trace) electrolyte) Looking at the previous equation and the results reported it can be asserted that the overall performance of the water-splitting cells is directly correlated to the intrinsic performance of the specific underlying PV sample. [1].
Figure 16. Comparison between direct and indirect water splitting and SFE plot in
KOH(red) and KPi (black) [1].

In Fig. 16A, the 3jn-a-Si PV solar cell was 7.7% efficient and yielded an overall PEC cell efficiency of 4.7% (Fig. 16A, black trace). We note that light passed through the mesh, which has a transmittance of ~85% (the efficiency reported here has not been corrected for light blocking by the mesh) [1].

Electrolysis efficiencies improved slightly upon operation of the cell in 0.1M KOH electrolyte because of an increase in catalyst activity (Fig. 16A); however, the use of this electrolyte resulted in a rapid and catastrophic decline in activity after 1 hour of photolysis.
(Fig. 16A, red trace), concomitant with visible dissolution of the 3jn-a-Si layer. This phenomenon had been previously observed and attributed to pitting corrosion of the ITO coating by the KOH electrolyte.

As shown in the figure the Co-OEC | 3jn-a-Si | NiMoZn cell exhibited significantly enhanced stability in borate electrolyte (Figure 16A, black trace) compared to the KOH solution which shows a slightly higher activity just in the first hour [1].

In order to have a better understanding of the co-catalytic system (Co-OEC + borate electrolyte) efficiency it’s also important to underline that the SFE may also be expressed as a direct product of the efficiency of the solar conversion of the PV cell \( \phi(PV) \), and fuel generation efficiency of watersplitting electrolysis, \( \phi(WS) \), which includes losses that arise from catalyst over-potentials and Ohmic resistances:

\[
SFE \ (\%) = \phi(PV) \cdot \phi(WS) \quad (2)
\]

Considering the wired set-up the \( \phi(WS) \) calculated happens to be ~60%. This value compares well with cell efficiencies based on 3jn-a-Si PVs in which the a-Si is isolated from the electrolyte [SFE = 6% for \( \phi(PV) = 10% \)] and for higher-efficiency systems using expensive PV materials [SFE = 18% for \( PV = 28% \)]. It’s pretty clear that higher overall cell efficiencies (>10%) may be readily achieved through the use of more efficient PVs. [1].
The wireless cell was constructed by directly depositing also the HEC (NiMoZn) onto the steelbacking substrate of the 3jn-a-Si cell as is shown in Fig. 3B with the overall device architecture of the wireless configuration of the device.

During the performance of the direct-wireless design it can be clearly seen that O2 bubbles evolved from the illuminated anode at the front face and bubbles of H2 evolved from the cathode at the back of the wireless cell.

To monitor this experiment, an Ar carrier gas was flowed over the headspace of the cell at a constant flow rate. The MS signal corresponds to the concentration of O2 in the carrier gas, which was used to determine the SFE for the wireless cell (see SOM for experimental details); a SFE = 1.75% was measured for a 3jn-a-Si solar cell with (PV) = 6.2%. Based on the PEC cell of (PV) = 7.7%, we expect that minimal efficiencies of 4.7% may be obtained from a properly engineered wireless cell.

### 4.5 CHAPTER CONCLUSIONS

The main functions of photosynthesis’ energy capture and storage can be summarized in an artificial device that performs water-splitting through an earth-abundant catalysts photoactivated by a semiconductor cell such as silicon-3jn. This possibility discovers new scenario where the Sun drives high energy reaction directly, with no use of
wires, under a simply engineered configuration. For example, the previously described design can be readapted from a PV configuration to a “standalone” device with (nano)particles in solution[1]. Furthermore this solar-to-fuels conversion process can be performed even without a membrane due to the low solubility of molecular oxygen and hydrogen into water. In addition the H2 produced by photochemical water-splitting could be directly stored and used or combined with carbon-dioxide reduction in a synthesized liquid-fuels processed externally to the cell [1]. This new scenario with this simple “stand-alone” device mainly constituted of semiconductor-based light collectors and earth-abundant catalysts, as the previously reported data provides describes can be considered the beginning of a low-cost systems required for a not expensive direct-solar-to-fuels systems.
CHAPTER 5

CO2 REDUCTION

As anticipated in the preliminary summary the core of this work comes from two other research projects: the water splitting performed by Nocera’s research group and the CO2 reduction performed by Salehi’s group.

In this chapter CO2 reduction will be discussed, in particular about the MoS2+EMIm-BF4 co-catalyst system which is one of the main ingredients of our final idea. The CO2 reduction, in fact, covers one of the two semi-reactions that will happen in the final set-up (Chapter 6). In this chapter an explanation will be given of this catalytic mechanism, on the catalyst performance and different function and role of each component of the co-catalyst system comparing the electro-catalytic with the possibility of a photo-catalytic system. Finally the efficiency of this system will be discussed and the parameter taken into account.

5.0 Initial Reflection

Today’s prospect of hydrogen being an efficient energy vector has motivated several works and studies on this subject as we explained and inquired in the previous chapters.
But the industrialization and commercialization of a ‘clean’ hydrogen-based fuel production, such as water electrolysis for hydrogen production and fuel cells for electricity generation by hydrogen, still represent a great challenge even if they have been increasing in the last decade, supported by strong policies and incentives mainly in developed countries.

Unfortunately the development and diffusion of this technology as the new energy solution faces two main obstacles: one more technical (already addressed in chap 2) low energy density of the hydrogen itself, and the other more socio-political and infrastructural because the adoption of this new way to produce energy requires a profound change in the current energy paradigm introducing the word in a completely new era with the necessity of modifications to the existing infrastructures for transport and energy utilization and production.

So an intermediate solution is clearly needed, an intermediate step that goes in the same direction but keeps usable the actual infrastructure and does not completely revolutionize today’s system.

The solution of this need can be found in the synthesis of hydrocarbon-based fuels from CO2 (i.e. captured CO2) which results in higher energy density vectors (up to 15 times more than hydrogen) which is also compatible with the existing infrastructures.
In fact this process not only could use the current energy supply-chain but it can also run using renewable resources for the energy required for the conversion (taking part in the carbon energy cycle shown in Figure 17) and it would also contribute significantly to the reduction of CO2 emissions.

Figure 17. Schematic of a potential carbon energy cycle for CO2-to-fuel conversion technology application.

Electrochemical reduction of CO2 is the strongest candidate to perform the CO2-to-fuel conversion at attractive energy efficiencies for industrialization as will be reported and explained further in this chapter.

Professor Salehi’s research group has designed a co-catalyst system which shows high faradaic efficiency for CO formation and almost negligible over-potential [36].

However there are still some weaknesses in the system that have to be addressed such as low current density (low turnover number) and the utilization of a high-cost noble metal (Ag) electrode.
This chapter will present this new low-cost co-catalyst system able to perform electro-reduction of CO2 at a much higher current density than previously reported, using a transition-metal catalyst and an electrolyte in 96 mol% of water solution. It will be explained how the system boasts selectivity for CO formation of up to 97.5%. In this chapter it will be first explained the behavior of this system in electocatalys mode will first be explained in order to better understand the transition to the photocatalytic systems introduced in the next chapter.

In fact applied potential affects the CO/H2 ratio production, so it’s an important and a potentially adjustable parameter for this new syngas production system.

In this first case the energy required for the reaction is the equivalent that can be directly provided by a 6-Watt solar panel. The output voltage of the photovoltaic unit is reduced by a DC/DC regulator and then applied to the reactor. In this configuration, there is no need for a DC/AC power inverter unit, which allows for a considerable cut in the overall costs.
5.1 **Carbon-Capture**

A significant enhancement in the reduction of the green house effect and in stabilizing current atmospheric CO2 concentration could be represented by the different carbon-capture systems.

Once captured, the CO2 can be either recycled (e.g. For enhanced oil recovery) or converted into high-energy density chemicals, following the renewable energy path and so representing a potentially valid and flexible way for storing excess.

The electrochemical reduction of CO to CO2 performed By Salehi’s Group is the best candidate in creating a final, effective and economically efficient CO2-to-fuel conversion at favorable energy efficiencies. One of the main reasons of the efficiency of this approach has to be recognized in the development of a cost-effective catalytic system that would perform the conversion at a low-overpotential, high current efficiency (faradaic efficiency), and high conversion rate (current density) [36].

This short analysis proposes a low-cost co-catalytic system which exhibits exceptional performance such as:

- negligible over-potential
- nearly 100% current efficiency
• the greatest current density reported thus far - for electrochemical CO2 reduction.

The integration of the system with the previously described Co-OEC and the a-Si 3jn provides promising results for effective continuous Direct Solar-CO2-to fuel (syngas) conversion.

Figure 18. Schematic of a potential carbon energy cycle for CO2-to-fuel conversion technology application.

5.2 Carbon-Utilization

As previously mentioned, the captured carbon dioxide can be also subsequently utilized (CCU). There are mainly two pathways of utilization for CO2. In the first one CO2 is not converted into other chemical forms, and it is directly used as solvent (e.g. In processing chemicals) or as a working fluid in various geothermal applications. Enhanced Oil Recovery (EOR) can be considered an efficient method of utilization for non-converted carbon dioxide: it has been estimated that 89 billion barrels of oil in the U.S. alone could
be recovered using the latest technologies for CO2-EOR, at the same time storing large amounts of carbon underground [15]. The second pathway for CO2 utilization includes biomass generation, and chemical and electrochemical conversion to other energy storage chemical forms. Algal pond systems for CO2 conversion to biomass represent the most economic methods to produce biomass on a large scale [16, 17]. In an algal mass culture pond system using different types of CO2 supply methods (such as bubbling or floating gas exchanger) at different volume concentrations, it is possible to obtain very high value products, mainly pharmaceutical or food grade products. Carbon is the dominant nutrient also in the case of biomass and biofuels production through photosynthesis microalgae bioreactors.

The potential of carbon dioxide conversion is substantial. In addition to biomass generation, CO2 can be used for production of fuels and chemicals such as syngas, formic acid, methane, ethylene, methanol and dimethyl ether. Although there are no cases of commercialized processes for CO2 conversion yet, the interest in this topic has been increasing in recent decades. A range of scientific and research areas have become involved, due to a higher shared awareness of problems related to GHG atmospheric concentration and global warming.
5.3 **Electrochemical vs Photoelectrochemical CO2 Reduction**

Since CO2 reduction has been a candidate for a valid and efficient method of CO2-to-fuel conversion electrochemical reduction of CO2 has been investigated extensively and it has been successfully achieved by Professor Salehi’s group. But it also important to take into account that the energy required for the reaction can be provided not only or indirectly from electricity produced by any kind of renewable source (i.e. Photo Voltaic panels) but also directly from solar light (photoelectrochemistry).

Although photoelectrochemical CO2 reduction is becoming an increasingly attractive option due to the potentially high efficiency of the process, characterized by the direct transfer of energy from the Sun without passing through electricity as a vector, this procedure hasn’t been performed yet because of the non negligible limitations in the choice of the photoactive catalyst (e.g. need of semiconductor electrode) so it still represents a challenge.

In order to be worthy of development the technology has to be applicable in a compact system, at room temperature and ambient pressure, with the possibility to scale up fairly easily. Moreover, the process has to be driven by a renewable source of energy (solar, wind, geothermal, hydroelectric, etc.), therefore operating as a renewable energy storage-mechanism.
To meet our main purpose we have to consider as the only source of energy to drive the reaction solar-light energy and or solar-thermal energy either for the photo- or the electro-chemical process.

In both cases the desired reaction products are an easily transportable medium for energy storage in the form of alcohol and fuel (HCOOH, CO, methanol, ethylene, methane) with attractive high recoverable energy density (compared to, for example, Lithium batteries, traditional batteries or flywheels) [18].

But, despite the listed positive aspects, even the DOE identifies the major obstacle for an efficient and effective CO2 conversion by electrochemical reduction as the lack of a catalyst capable of achieving selective break of C-O bonds in carbon dioxide, using earth’s abundant sources of energy, and low-cost reducing agents [19] especially considering that an optimum catalyst would show high energy efficiency (low overpotential), high current density (high rate of reaction), high faradaic efficiency (F.E.) for the desired product (catalytic selectivity), and a long lifespan.

So our solution to the problem, as long as we are not able to produce such CO2-photo catalyst, is to shift the photo-active problem from the CO2-reduction side of the reaction to the OER side.
5.4 **Thermodynamic and Kinetic Considerations on CO2 reduction.**

It’s well known that CO2, carbon dioxide is a stable molecule, thermodynamically and kinetically.

So in order to perform its reduction to CO multi-electron steps with proton coupling are required, since more thermodynamically stable molecules are obtained.

Getting deeper in the kinetics of the reaction we discover that it’s not that straightforward due to the fact that the reaction involves the formation of an intermediate complexes (CO2*) that occurs at much higher potentials so that the actual potentials have to be much higher than the thermodynamic potentials showed in Equations 3.1-3.5 (below). In 1969, Paik et al. were the first to propose that the reaction for CO2 conversion is preceded by the formation of an intermediate complex (CO2*) [20]. Later we will explain the role of this one-electron reduction intermediate in the interaction with the CO-catalyst and its responsibility in the low reaction rate as well as the high over potential required for the reaction (Equation 3.6 below) role confirmed by the use of spectroscopic techniques. Benson et al. Identifies two main pathways in which CO2 chemical bonds can be broken to promote the formation of more complex and energetic molecules [21].

The conversion of CO2 into a mixture of CO and H2 (also called syngas or synthesis gas), is basically a direct production of fuel that can be used immediately in a
syngas engine, or utilized as an intermediate for production of ammonia and methanol, or converted to liquid fuels through the Fischer-Tropsch process.

<table>
<thead>
<tr>
<th>Chemical Equation</th>
<th>Standard Potential $E^0$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$</td>
<td>$E^0 = -0.53 , V$</td>
<td>(3.1)$^a$</td>
</tr>
<tr>
<td>$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H$</td>
<td>$E^0 = -0.61 , V$</td>
<td>(3.2)$^a$</td>
</tr>
<tr>
<td>$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O$</td>
<td>$E^0 = -0.48 , V$</td>
<td>(3.3)$^a$</td>
</tr>
<tr>
<td>$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$</td>
<td>$E^0 = -0.38 , V$</td>
<td>(3.4)$^a$</td>
</tr>
<tr>
<td>$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$</td>
<td>$E^0 = -0.24 , V$</td>
<td>(3.5)$^a$</td>
</tr>
<tr>
<td>$CO_2 + e^- \rightarrow CO_2^{--}$</td>
<td>$E^0 = -1.90 , V$</td>
<td>(3.6)$^a$</td>
</tr>
</tbody>
</table>

The electrochemical reduction of CO2 into CO and H2 involved in the first pathway is the ‘easiest’ conversion from a thermodynamic and kinetic perspective: the Nerst potential for formation of CO is the lowest (see Equation 3.1) and the reaction involves ‘only’ two electrons. Moreover the electrochemical conversion is hydrogen-proton coupled and in most cases H2 formation occurs as a concurrent reaction. The second pathway is more challenging from the kinetic point of view, and it implies the direct formation of liquid fuels through the electrolysis process. In this case, four-six and eight-electrons charge transfer is required for the formation of the desired products. However, in both the paths described the functionality of the catalyst and the medium for the reaction is of main importance. The distribution of the products (catalytic selectivity) and the
efficiency of the reaction (current efficiency and overall energy efficiency) strongly depend on the selection of the catalyst and the medium.

5.5 **Heterogeneous Electroreduction of CO2 in Aqueous Medium.**

It’s important to underline that in aqueous mediums there are two reactions competing:

- Hydrogen evolution reaction (HER)
- CO2 reduction.

Horiand Suzuki reveals that at a given fixed potential, HER rate is proportional to the pH (proton activity) of the electrolyte and indeed is prevalent in acidic solutions [22]. To increase the faradic efficiency of the CO formation we just have to increase the overvoltage and thanks to that hydrogen evolution gets usually, but not always, suppressed favouring the formation of the desired product (CO, HCOOH, CH4, etc.).

Hydrocarbons and alcohol formation at Cu electrodes has been extensively studied and reported in last 20 years [23,24,25], and there are excellent reviews on the literature [26,27,28].
The Faradaic efficiencies gets to 70% for the production of hydrocarbons, result reported in potassium bicarbonate solution (0.1 M KHCO3) and at reasonable reaction rates (up to 7 mA/cm2 current density) [29].

But the multi-step characteristic of the reaction kinetics implies that high negative potentials (low energy efficiency) are required for the reduction (-1.4 V vs. SHE) [29].

We can get a faradaic efficiency close to 100% for the formation of formic acid HCOOH in a lithium bicarbonate solution, but at low current density (?0.3 mA/cm2) [20] which was firstly discovered by Eyring’s group in 1969. Further development took current efficiency for formic acid formation was high (94%) but at the expense of a negative cathode potential (-1.56 V vs. SHE).

Current density was still low at standard environmental conditions (0.6 mA/cm2) but they showed how it is possible to enhance the reaction rate by increasing temperature and pressure in the reactor, maintaining high current efficiency. Hori et al. reported higher current efficiency (97.5%) at higher current density (5 mA/cm2), running an experiment at room temperature in 0.1 M KHCO3.

Several other studies have been carried out with the aim of developing Au- or Ag-based catalyst for high energy efficiency CO2 reduction [30,31,32]. The reaction at Au and Ag electrodes not only occurs at low over-potential, but is usually associated with high current density, high current efficiency, and relatively high stability of the catalyst in time.
But as we have already said in the economic section we are looking for a cheap highly manufacturable solution based on earth abundant material so the use of these metals (valid in general for all metal electrodes) have:

- too costly (especially for noble metals)
- Problems with corrosion
- Problems related to deactivation or passivation of the catalyst in long-term electrolysis.

5.6 **Electroreduction of CO2 to CO at Ag Electrodes in EMIM-BF4 Ionic Liquid**

5.6.1 **Ionic Liquids.**

Salt in a liquid state, the Ionic liquids have found in the last two decades among both academic and industrial fields a continuing growing interest. The great focus on them is mainly justified by wide range of uses and applications such as powerful solvents, as thermal fluid for heat storage, and as electrolytes. Our interest narrows its attention to this last interesting role: electrolyte. Ionic liquids, most of them, have attractive properties for electrolysis applications, compared to traditional ionic liquids and other ordinary liquids (such as acids or water solutions) because of these main features:

- low vapor pressure
• high ionic conductivity (in the range of aqueous electrolytes values)
• the ability to behave as a catalyst

These properties make new ionic liquids suitable solvents for electrochemistry, in contrast with volatile organic solvents and their inherent environmental-related problems [33,34,35].

5.6.2 **EMIM-BF4 electrolyte for CO2 Reduction.**

In the setup of the continuous flow CO2 reduction system by Professor Salehi’s group a very specific Ionic Liquid (IL) has been chosen for some very specific behavior in the CO2-to-CO reaction. 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF4 chemical structure is shown in Fig 28) ionic liquid in a flow reactor has been demonstrated to enhance the electro-catalytic properties for CO2 conversion by reducing the energy barrier for the formation of CO and so behaving like a co-catalyst because of its fundamental support role in the thermodynamic of the reaction. The high selectivity for carbon monoxide production was given by the utilization of silver as the working electrode (cathode).
Figure 19. Chemical structure of 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIM-BF4) ionic liquid.

Of a great interest is the fact that not only was a negligible over-potential for the reaction (0.17 V) observed, but also high current efficiency and quite high robustness of the system over time. Over 96% F.E. reported in a 7 hour-long experiment. It was proposed that the use of this specific ionic liquid would facilitate the formation of a complex between the cation of the electrolyte (EMIM+) and the CO2* intermediate. The formation of the complex (EMIM+ CO2*) would occur at low cathode potential (-0.25 V vs. SHE) thereby drastically reducing the energy barrier for CO2 reduction [36].
Figure 20. Schematic of free energy path for formation of CO in water or CH3CN (solid line) and in EMIM-BF4 (dashed line).

This choice and the consequent constitution of a co-catalyst system (EMIM-BF4 electrolyte + Ag cathode) can be considered a breakthrough in the CO2-to-fuel conversion via electrochemical reduction.

Energy efficiencies of up to 87% percent for CO production have been reported, making this electro-catalytic system a suitable candidate for possible scale-up applications. We can summarize the co-catalyst role of EMIM-BF4 electrolyte in these 3 main functions:

• Electrolyte

• Driving almost to zero the energy of formation of CO2*- 

• Inhibits HER
5.6.3 **CO2-to-fuel CO-CATALYST System: MOS2 + EMIMBF4 Aqueous Solution**

Molybdenum disulfide (MoS2) is an inorganic compound belonging to the transition-metal sulfides group, commonly used in different technological sectors, mainly in lubrication, electronics, has driven the attention of the scientific community thanks to its catalytic applicability (e.g. hydrodesulfurization in petroleum refining) and its attractive chemical and physical properties. Recent works demonstrated remarkable properties of nanostructured MoS2 for photo- and electro-chemical water splitting, making it an inexpensive substitute for platinum in hydrogen production from water electrolysis [37].

This is the main catalyst chosen by UIC group to drive the electrochemical conversion of CO2 into syngas.

In order to investigate the electro-catalytic properties of MoS2 for CO2 reduction, cyclic voltammetry (CV) and chrono-amperometry (CA) were performed in a standard three-electrode electrochemical cell (see Methods and Materials). Impressively, the bulk MoS2 catalyst showed 60 times higher current density than a bulk Ag catalyst at a cathode potential of -1.0 V vs. SHE [36].

Moreover, the experiments were carried out in a less concentrated (and therefore lower cost and more environmentally friendly) ionic liquid solution in water (4 mol%
EMIM-BF4, 96 mol% H2O), compared to solutions previously reported. To emphasize the importance of the results, Table I presents a comparison between MoS2 and Ag catalysts according to the experimental results of both this paper and previous publications. It is also interesting to notice that the Ag bulk catalyst shows almost 0% catalytic selectivity for CO production in the low concentrated 4 mol% solution, indicating that the entire current efficiency is utilized for hydrogen evolution. On the other hand, if silver nanoparticles (Ag NPs) are used rather than bulk silver, the current efficiency for CO formation shifts from \(~ 0 \%\) up to \(~ 80 \%\) [38].

**TABLE I. COMPARISON OF CATALYSTS FOR CO2 REDUCTION IN EMIM-BF4 SOLUTIONS AT -1.0 V vs. SHE.**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Current Density (mA/cm²)</th>
<th>Electrolyte</th>
<th>CO F.E.</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoS₂ Bulk</td>
<td>60</td>
<td>4 mol% EMIM-BF₄</td>
<td>97.5 %</td>
<td>d</td>
</tr>
<tr>
<td>Ag NPs (&lt;50nm)</td>
<td>7</td>
<td>4 mol% EMIM-BF₄</td>
<td>(~ 80 %)</td>
<td>[71]</td>
</tr>
<tr>
<td>Ag Bulk</td>
<td>3</td>
<td>4 mol% EMIM-BF₄</td>
<td>(~ 0 %)</td>
<td>d</td>
</tr>
<tr>
<td>Ag Bulk</td>
<td>1</td>
<td>18 mol% EMIM-BF₄</td>
<td>96-98 %</td>
<td>[68]</td>
</tr>
<tr>
<td>Ag NPs (5nm)</td>
<td>0.8 (^b)</td>
<td>75ppm water (^c)</td>
<td>96-98 %</td>
<td>[61]</td>
</tr>
</tbody>
</table>

\(^b\) max. current density -1.2 mA/cm² at -0.75 V vs. SHE.  
\(^c\) at higher water concentration would show higher current density.  
\(^d\) experimental work for this paper.
Other relevant results emerged from the electrochemical cell experiments. Firstly, the onset potential for CO formation was observed to occur at -0.5 V vs. SHE, just 0.17 V higher than the thermodynamic potential for CO formation in a solution of pH 4 (-0.339 V vs. SHE). Secondly, it was observed that production of CO/H2 increases/decreases when the potential is switched from -0.5 V to -1.0 V vs. SHE.

Because of the competing nature of HER with the CO2 reduction reaction usually in the context of electrochemical CO2 reduction, hydrogen is often considered an “undesired product.” The main reason is that if hydrogen evolution occurs it means that part of the energy needed for the reaction is “stolen” for the formation of H2 molecules.

As we already mentioned before the Faradic efficiency could vary according to the over-potential and so to the concurrent production of hydrogen during the reaction, the system here reported the presence of a singular property associated to this phenomenon. The ratio between CO and H2 formation can be easily regulated by varying the cathode potential applied to the system.

At the same time no other products were detected (or were present in less than 3 ppm, the detection limit of the GC) for the duration of the reaction, resulting in a clean process from this point of view. This promising result could represent an enormous advantage in the prospect of an industrialized process for the conversion of captured CO2 into fuel (syngas in this case). The CO/H2 ratio production can be adjusted according to
the syngas required for any given application (i.e. for Fischer-Tropsch Synthesis the CO/H2 composition ratio of syngas can vary between 0.5 and 1, depending on the catalyst utilized).

![Figure 21. Faradiac efficiency plot.](image)

5.6.4 **CO2 Reduction co-Catalyst systems Results and Conclusions.**

In the batch experiments carried out a few months ago with a three-electrode electrochemical cell at a low concentration of IL, water (90 mol% H2O) solution concentration, the catalyst activity in terms of conversion rate (current density), even if it was expected to decrease about 30%, exhibit a greater current density for CO2 reduction than what is reported in previous literature. So it has been reported by prof. Salehi’s
research group that by applying a cell potential of 4 V a stable behavior is obtained even in the continuous flow process, with steady cathode potential at -1.6 V and steady current density at 40 mA/cm².

To verify the CO presence in the processed gases, after 10 minutes, a 1 mL sample was injected into the GC for detection showing a clear H₂ peak and CO peak visible at 1.8 min. and 8.8 min. of detection, as reported in (Figure 21). To have a clear and fair understanding of the detect results reported it must be said that having bigger peak areas for O₂ and N₂ with respect to CO and H₂ does not reflect the actual amount of air molecules was higher than the amount of syngas molecules.

Only after calibration of the Gas Chromatograph for the different gases will it be possible to judge the actual volume composition of the sample.
Figure 22. Peaks of gasses detected by GC.

For comparison, the system was run again but substituting the MoS2 catalyst with an Ag catalyst (Ag NPs, 100 nm av. dia.) at the cathode. A similar GC detection curve trend was observed, but with CO peak areas at least 3 times smaller than MoS2 case. Similar results were obtained also changing the cell potentials from 4 V to 3.5 V and 3 V.

From the data just reported it can be certainly asserted that the results obtained with this co-catalyst system are promising but there is still another big step to make this system
completely auto-sufficient: passing from an electrochemical reaction to a photochemical one.

The MoS2 catalyst performance for CO2 reduction in a batch electrochemical process in terms of over-potential, current efficiency, and current density are certainly excellent so it’s the best candidate to drive the reaction. The only challenge left is create a system that provides the required over-potential using the Sun energy. Syngas, the end product of the process just described, is currently manufactured through gasification of fossil based carbonaceous materials, in which coal is injected in high-pressure gasifiers that at high temperatures (>700°C) produce the constituting gas mixture of syngas. Using the gasification process would comport all the downside exemplified in chapter 1 and 2 plus even if the gasification is well known and several plants already operate at industrial scale, the production of syngas through gasifiers is still an under-developed and high-cost technology.

The use of this new way to transform CO2 into syngas can represent a valuable, energy-favorable, and environmental-friendly method for production of syngas.

But to see whether this system can compete in terms of energy efficiency and production rate, few other steps have to be accomplished. One of them is definitely to be able to scale-up the system in order to reach a significant production rate (in terms of gas products flow rate).
But probably the first and most important step to make is to increase the overall efficiency; this can be definitely achieved minimizing the losses inside the single cell but probably the greater efficiency improvement is in the input energy: It must be said that the cell potential applied is still too high for the system to represent an energy-efficient and competitive setup for fuel production by CO2 reduction especially because this input is not for free. Another source is needed. The next chapter will focus on solving this problem, making this system completely energetically auto sufficient driven only by the most abundant and environmentally friendly energy source that we have: the sun.
CHAPTER 6

THE PATH TO A NEW-SET UP

In this chapter the discussion will include the new set-up used to perform the direct-photo-CO2 reduction, storing Solar Energy in the form of Syngas while CO2 is reduced, performing the solar-to-fuel transformation that we have discussed in the previous chapters.

As stated in the preliminary summary, the core of this work comes from two other studies: water splitting by Prof. Nocera’s research group and CO2 reduction by Prof. Salehi’s group. Here, we combined the two concepts into one new very multifunctional and versatile device.

In this chapter, the built in potential of the 3jn explained in Chapter 3, the Co-OEC illustrated in Chapter 4, and the MoS2+EMIM-BF4 co-catalyst system described in Chapter 5, will be used to create a stand-alone device that can transform water and CO2 into CO+H2+O2 (syngas+O2) using only light impulse.

The mechanism behind this new cell, the different configuration that could lead to this result, the problems and solutions encountered throughout this research, as well as the history of the set-up production and adjustments will be discussed here.
Finally the conclusive design and its production process will be explained with the different functions and configuration that it can perform.

6.1 **One-Chamber With a-Si-3jn Fully Immersed + 2 Catalyst.**

Instead of using a potentiostat or any artificially generated potential difference, I have chosen to employ the over-potential driven by shining 1 sun (1.5 AM) on the a-Si-3jn. In this way enough potential can be produced to enhance the Co2-reduction reaction or the watersplitting reaction (previously described).

In order to obtain this goal it has been chosen to deposit Mo2 as the cathode catalyst and the Co-OEC as the anode catalyst.

Exactly like in the batch process described in chapter 4 and 5 either water or diluted Ionic Liquid (EMIM-BF4) will be used as the electrolyte in order to perform water splitting or Co2 reduction.
6.1.1 **Conceptual Mechanism.**

The idea here is to use the built-in potential to drive the two reactions on the two sides of the artificial leaf. We know that the a-Si-3jn can generate between 1.8 and 2.2 V with a direct exposure of 1 Sun (1.5 AM). Of course behind a glass and inside a liquid we are expecting some losses due to reflection and diffraction, but since we need just 0.9 V to start the Co2 reduction we are confident that the driving potential will be enough.

![Diagram of Fully immersed CO2 reduction scheme](image)

*Figure 23. Fully immersed CO2 reduction scheme.*
6.1.2 **Fully Immersed CO2 Reduction.**

The idea here is to use the built-in potential to drive the two reactions on the two sides of the artificial leaf. Knowing that the a-Si-3jn can generate between 1.8 and 2.2 V with a direct exposure of 1 Sun (1.5 AM), it’s a direct consequence that behind a glass and inside a liquid it is expected to suffer some losses due to reflection and diffraction. But, since the minimum potential needed to start the CO2 reduction is just 0.9 V it can be confidently asserted that the driving potential will be enough.

![Diagram of CO2 reduction reactions scheme](image)

Figure 24. CO2 reduction reactions scheme

According to this theory, the chemistry behind the two reactions should be exactly the same as the one in the electrochemistry batch process described in the 4th chapter.
In the figure above, we use a schematic description of the reaction on the two surfaces of the 3jn covered by the two catalysts previously analyzed (MoS2 cathode side and Co-OEC anode side) all immersed in a 50% volume solution of EMIM-BF4 ionic liquid and deionized water all saturated with Co2.

6.1.3 Fully Immersed Water-Splitting.

This scheme recalls exactly the same configuration described in the direct to fuel water splitting described in chapter 4. There is no difference in the principles or in the configuration. The only difference here is the use of the MoS2 as cathodic catalyst instead of the NiMoZn adopted by Nocera’s group. Since MoS2 is a highly qualified candidate for HER, it is more than suitable not only for CO2 reduction but also for water-splitting.

\[
\begin{align*}
2\text{H}_2\text{O} & \rightarrow 2\text{H}_2 + \text{O}_2 \\
4\text{H}^+ + 4\text{e}^- & \rightarrow 2\text{H}_2 \\
\text{P}_2 + 4\text{H}^+ + 4\text{e}^- & \rightarrow 2\text{H}_2\text{O} \\
E_{\text{cathodic}} & = 0 \text{ V} - 0.059 \text{ (pH) V vs NHE} \\
E_{\text{anodic}} & = 1.23 \text{ V} - 0.059 \text{ (pH) V vs NHE} \\
E_{\text{net}} & = -1.23 \text{ V}
\end{align*}
\]

Scheme 1.
6.1.4 **One-Chamber-Diversified Immersion CO2 Reduction.**

Figure 25. Fully immersed water splitting scheme

Figure 26. One-chamber-diversified immersion CO2 reduction scheme
In order to avoid the contact of the a-Si-3jn with the acid electrolyzer and avoid any losses due to reflection or refraction, it has been chosen to insulate the 3jn from the acidity of the electrolyzer used for Co2 reduction (EMIM-BF4) and directly expose the 3jn surface to the light.

To achieve this result, the new design is characterized by one chamber filled with 50% in volume diluted EMIM-BF4 saturated with Co2. The artificial leaf’s surface is made of the 3jn+stainlesssteel wafer with the stainless steel as oriented to the inside of the chamber and the 3jn to the outside directly exposed to the light. The last modification from the previous set up design consists of a wire that connects the external surface of the 3jn to the internal solution of the chamber.

6.2 **Two-Chamber Cell: Co2 Reduction+Water-Splitting.**

Combining the two reactions into one set-up it is possible to simultaneously perform the Co2 reduction, the Hydrogen evolution and the oxygen evolution reaction directly using the same 3jn exposed to 1 Sun (1.5AM).

Knowing that the p-doped-side of our artificial leaf, coated with Co-OEC, behaves like an anode while the stainless-steel-side, coated with MoS2, behaves like a cathode the same result of a two distinct electrodes can be obtained by just positioning the a-Si-3jn as
a separator of the two different chamber exposing the anodic side of the artificial leaf to one chamber and the cathodic part to the other:

- the anodic one containing water
- the cathodic one containing diluted ionic liquid saturated with CO2

In order to close the electrochemical circuit and allow the ions to move from one chamber to the other, an ion transfer membrane is also required as a separator of the two chamber of the cell.

Figure 27. Two-chamber scheme
6.2.1 **Double Chamber Cell Design.**

The design is made up of 4 different pieces with a total of 7 pieces in the assembly:

- 2 frames (red)
- 2 glasses (transparent)
- 2 slides (blue)
- 1 body (grey)

Figure 28. exploded vision of the set up design
Each type has a different function:

**Frames**: their main function is holding and sealing the glass to the two main faces of the body. In order to improve its impermeability, adhesion and stability, a series of screws, a rubber coating and silicon glue where used to seal everything. (The material used, the type of coating and sealing material specification will be explained in the Material and Production section.)

**Glasses**: their main function is letting the light pass through and hit the a-Si-3jn. They are used to seal the cell from the outside. The main concern about the glasses has been about their optical properties. Since the 3jn has an absorption range of 1 sun it is important to ensure minimal losses due to lack of transparency in the glass.
**Slides**: their main function is dividing the set up in two completely sealed chambers and holding and sealing the a-Si-3jn (coated with the two catalyst on the different faces) and the ion transfer membrane as the separation membrane for the set up. [In order to improve their impermeability, adhesion and stability a series of screws, a rubber coating have been used and finally everything has been sealed using silicon glue. (the material used, the type of coating and sealing material specification will be explained in the Material and Production paragraph)]. This is one of the most important pieces of the entire set up. It holds what we can call the actual artificial leaf. It divides the two chambers while allowing only to ion to pass through in order to close and properly divide the reaction circle. However, its functions aren't only limited to these main two; it also makes possible the monitoring and the communication of what happens inside the set up or on the membranes.

**Body**: its main function is to hold the set up together and completely seal the two chambers. It also contains the two electrolyzers , each one in its own chamber separated by the slides which slide into the Body.holding and sealing the a-Si-3jn (coated with the two catalyst on the different faces) and the ion transfer membrane as the separation membrane for the set up. [In order to improve their impermeability, adhesion and stability a series of Figure 39. Slides top view with holes function screws, a rubber coating has been used and finally everything has been sealed using silicon glue].
6.2.2 **Redesign to Increase the Voltage: 3jn in Series.**

The main aim of this modification of the initial design is to create a system with higher cell potential by putting in series multiple 3jn. The main difference in the set-up assembly is substituting one of the two slides with the 1/2 slide showed in Fig 41. Also, another possible method is to put in series more than two 3jn without changing any piece of the set-up. But for a more didactic and clear understanding of the improved mechanism it’s easier to start with just two junctions.

From the physical point of view to better understand this improvement, it’s necessary to exemplify the scheme with a more common example which fairly reflects the
new structure. A fair analogy is to compare the 3jn with the classical battery; the main
difference is that in order to activate the a-Si-3jn a direct light excitation is required.

Putting two 3jn in series gets the exact same results of putting two batteries in
series, the overall potential is the sum of the two diminished by the losses.

![Diagram of 3jn in series](image)

Figure 31. 3jn in series viewed like batteries in series

As was explained in Chapter 3, the built in potential for a single 3jn excited by 1
Sun (1.5 AM) is between 1.8 and 2.2 V, so putting two 3jn in series (considering a zero
loss) between 3.6 and 4.4 V built in potential can be expected. To be conservative and take
into account the losses caused by the ohmic contact, a fair expectation is 3.5 V. This built
in potential will give more than enough potential to drive an efficient reaction for both Co2 reduction and watersplitting.

Figure 32. Four main view of the slide with a two-3jn in series configuration.
To have a clear representation on how to arrange the two 3jn in the set up the different faces have been highlighted in different colors so that their different roles and coatings will be clear.

The purple and green surface are both exposed to the light and are both the p-doped side of the a-Si-3jn while the red furnace represents the stainless steel substrate on top of which the 3jn wafer gets deposited, which also does not get directly hit by the light.

The main difference between the purple and green surface is in the role and the coating. The purple surface is the upper one and it gets coated with the Co-OEC so it is directly in contact with the water electrolyzer solution. The green surface, even if it has to get hit by the light to get activated, can't be in direct contact with the solution in order not to short circuit the “purple battery” potential so it gets coated with a hydrophobic coating. For this same reason, in the back side of the cell only one of the two red surface is directly exposed to the IL water solution and it is the one that corresponds to the back triple junction (green front) and this one is the only one that gets coated with the CO2 reduction co-catalyst (MoS2). So that the only two surfaces in direct contact with the solutions are the front of the front junction and the back of the back one, which are the only ones with activated catalyst on them in order to have the reaction “closing” the circle including the higher difference of built-in potential.
6.2.3 Multiple Use of the Design.

The new set up has been designed in a way that can perform multiple different experiments. With this design the following, can be performed:

1. fully immersed CO2 reduction configuration
2. fully immersed water splitting configuration
3. one-chamber-diversified immersion CO2 reduction configuration
4. two-chamber cell: diversified immersion CO2 reduction/water splitting configuration
5. redesign to increase the voltage: 3jn in series configuration

The versatility of the set up is given by the possibility to easily pass from one chamber to another cells by just putting the anion transfer membrane in the smaller window of the slides.

The possibility to slide the 3jn in and out, given by the slides, allows different arrangements and a fairly rapid change of the “artificial leaf”. Also the double glass window not only allows a future double side shining of the light source but also a constant monitoring of thebobbling activity on the two sides of the artificial leaf.

The fully immersed CO2 reduction or water splitting configuration can be achieved by allowing communication between the two chambers and leaving open the membrane window, creating a one chamber configuration. The artificial leaf will be held by the slides recalling the scheme of section 6.1.2 and 6.1.3.

The one-chamber-diversified immersion CO2 reduction configuration can be achieved by closing all communication between the two chambers. A completely impermeable membrane will fill the membrane window, creating a double isolated chamber configuration.

The artificial leaf will be held by the slides (recalling the scheme of section 6.2) then the chamber corresponding to the OER will be left empty while the CO2 reduction
chamber will be filled with the electrolyte saturated with CO2. To guarantee both anode and cathode presence inside the solution and in order for the reaction to happen, a wire has to connect the anodic side of the artificial leaf (the one directly exposed to the light) and the electrolyte working as an anode.

The two-chamber cell diversified immersion CO2 reduction/water splitting configuration is the configuration that most motivated this design. [It can be said that the set-up has been initially designed for this configuration]. This configuration will be achieved by putting the anion transfer membrane in and also in the “artificial leaf” opposite window.

The two chamber configuration will be achieved and only H+ will pass from one chamber to the other as explained in section 6.3. The wire holes will be used only to monitor the cathodic, anodic and cell potential.

The 3jn series configuration will be achieved by arranging the set up in the exact same way of the wo-chamber cell configuration, the only difference being in the rearrangement of the 3jn in series as explained in the 6.3.3 paragraph.

As we can see, this design can be used in a very wide range of experiment configurations and, as previously stated it has been seen that not only the ones that require one side illumination but a much greater number of applications can be reached using a photo-active catalyst on both sides.
6.2.4 **Material and Production.**

The materials used were inexpensive and highly manufacturable. The time constraint has been our second issue in the production of the final device. The design was finalized by the end of February and the production was started in March. In order to have a working set up in April, the choice of production was planned towards the fastest and cheapest way to produce the 5 pieces required to assemble the set-up.

Using a fairly new technology such as the 3D printing, we have been able to meet our requirements. The material used for the pieces is ABC plastic, a fairly resistant thermoplastic material. The only issue in this production has been that the only printer available was a printer that did not guarantee the complete sealing of the pieces produced.

In order to properly seal the set-up, we coated each and every piece with rubber paint Latex paint and hydrophobic coating. We completed the sealing with silicon glue once the entire set up was assembled for running the experiments.

The two frames are attached to the body using 16 #3 screws for each face. The glass used is a GE 124 type and the transmittance curve is reported here.
Figure 34. transmittance curve of GE 124

As is shown, almost all the sunlight emitted by the sun can pass through this type of glass.

This guarantees a minor loss in the absorption required to the 3jn to build the photoenhanced potential.

The slides are connected by another series of 12 flat head #3 screws insulated from the environment by a thin film of silicon glue. The 3jn and the anion transfer membrane are sealed with another addition of silicon glue.
6.3 History of Progresses & Issues Of The “New Artificial Leaf Set-Up”.

Starting with the idea of finding the intermediate step to fully renewable energy production, it has been decided to merge two systems with great potential into a more versatile system: the Figure 43. transmittance curve of GE 124 CO2 reduction co-catalyst system and the direct water splitting 3jn+ Co-OEC system. This has become the direct photo reduction of CO2 into Syngas.

As described in paragraph 6.1, the first option explored was the “one-chamber cell with a-Si-3jn fully immersed + 2 catalyst”. This design has a great potential: in the solution there is everything needed for both of the reactions to happen on both sides of the 3jn, the built-in potential should be enough to drive the semi-reactions and both catalysts are active in that environment.

The main focus, because it has never been done before, is on the CO2 photo-reduction. Trying several times with this approach the result, wasn’t the one that was expected.

I just started reproducing the batch process experiment described in chapter 5 using the 3jn as cathode just to test the response of the catalyst on this new substrate. After testing the electrochemistry capability of this new system we repeated the test with a
photocatalytic approach. A very intense activity has been noticed on the MoS2 side, a lot of bubbles have been produced but the result wasn’t the one expected. Only hydrogen was produced and the system started to fail after 15 min of activity.

Figure 35. batch process photochemical test.

The hydrogen production was definitely a good sign, proving that there were catalytic activities in the system, though it also meant that there was not enough voltage to perform CO2 reduction.
The first guess was that the surface area of the 3jn wasn’t large enough to produce the required potential to perform CO2 reduction while it was enough for HER. The surface of the 3jn used in that batch experiment was between 2 and 3 cm\(^2\) because that was the maximum capacity of our set up at that time. After further investigation, it was found that the main problem in this design, the one that caused the failure of the leaf in less than an hour was the acidity of the IL environment which attacked the zinc oxide, positioned under the 3jn, progressively detaching the 3jn from its substrate causing the loss of its ohmic contact.

Several contingency methods have been adopted in order to avoid the destruction of the “artificial leaf” but, so far, none of them has completely solved this issue.

One of the ideas tried to solve the acidic attack to the 3jn was using a protective coating. The requirements for this protective coating are:

- transparency
- high conductivity
- acid resistance
- not a co-catalyst

We first thought about gold but, even a nano layer of gold has too high of a reflective coefficient to let enough light to pass through getting absorbed by the 3jn.
Furthermore, gold would have actively participated with the reaction and it would have been too hard to define which catalyst was the one in charge of the reaction performance.

Figure 36. before and after acidic exposure of the 3jn.

Probably the best coating available was graphene due to its high conductivity, transparency, and the fact that it’s a very inert material. The only issue with graphene was the transfer process. Once graphene is grown, it can be transferred on to a wide range of substrates but the main forces that keeps the graphene in place on top of the substrates are Van der Waals forces. In the test that have been performed to evaluate this coating behavior in our acidic environment, it has been found that in our I.L. solution the Van der Waals forces are not enough to keep the graphene in place. Because of this, this approach was also not successful.
Because of the short time and resources, the research for an appropriate coating stopped with graphene and therefore another approach has been adopted.

Since the Zn oxide is positioned between the stainless steel and the actual 3jn, instead of coating the entire artificial leaf, it was decided to protect only its edges so that the acid solution couldn’t penetrate under the 3jn and the entire system could last longer.

This test was performed using epoxy as protection for the edges and some improvement has been reported but still it was not enough for a stable and lasting system.
Figure 38. before, after 5 min, after 15 min exposure to the IL of epoxy protected 3jn.

At this point the decision was made to change the design in order to avoid this “acidity” issue. This was the cause for the “one-chamber-diversified immersion” design described in paragraph 6.1.4. In this design, the direct contact of the 3jn with the acidic media is completely avoided and the functionality of the 3jn is kept untouched.

The first attempt to build this design was made with home materials, attempting to make it as cheap and manufacturable as possible. The result is reported in the next figure.

This set up gave me a first sense of what direction to take, it was just a trial but I think it has been very helpful in understanding which are the main issues to fix and what are the strong points of this idea not only on paper. With this poorly manufactured design we were able to produce Hydrogen and detect some activity around the time where the CO
peak was expected but there was never a clear signal of its presence. But even this was not an easy result to achieve. During the preparation of this cheap prototype I had to face major linking problems, voltage monitoring issues and internal pressure complications. The use of silicon glue was fundamental to ensuring its proper sealing. Monitoring the cell potential and the cathodic potential wasn't easy. I had to perform different trials positioning silver electrodes in order to get an acceptable voltage and often the numbers were too far from our predictions. Plus, while the cell was running, because of the internal gas production and the progressive increase of temperature, the internal pressure of the set-up caused relevant gas loses. We were able to address this problem using buffer air bags to collect the excess of gas produced while performing the experiment.

Figure 39. arranged set-up
The transition to a better manufactured set-up was necessary in order to collect consistent and reliable data. So the production of a more complex and versatile set-up was the subsequent step.

Because the initial idea was to produce a device that is small, cheap and fast to produce and to assemble, in a “Mc Dolnald” type of production I chose the cheapest and fastest way available: 3D printing.

Using 3D printing we managed to produce the 5 pieces described in the 6.3.2 paragraph but the challenge wasn’t concluded. One of the main difficulties was sealing it properly. Because of the high volatility of CO, even a minor leakage can cause failure in the detection during Gas Cromatography.

In order to have a perfect seal and no interaction between the substances, we used several coatings and sealants quoted in the material production session. They were chosen to be inert but also to be able to fill the porosity of the material. the set up was first painted with a peelable rubber coating than covered with a two step hydrophobic paint. After few experiments a minor crack occurred and it was filled with a latex paint.

Another major drawback that needs to be reported is a disassembly problem which caused the irreparable damage of the slides. In the initial design there was not enough play and the roughness of the pieces, even if treated and polished, were too much so a redesign of the slides was necessary for an optimal assembly and disassembly procedure. They were
reprinted with some modification and the addition of two aluminum pieces to facilitate the sealing and the disassembly. The aluminum intermediate avoided the plastic to plastic contact decreasing adhesions between the surfaces once sealed with silicon glue. The results were successful and the set-up now can be used multiple time without the risk of damaging its structure.

Figure 40. New set-up while working.

Once the set-up had been produced and finalized it was possible to run several experiments.
The configuration adopted so far has been just the double chamber but with different triple junction arrangements. One, two and three junction in series were tried. The results and the conclusions will be discussed in the next chapter.

Figure 41. two and three 3jn in series.

One more thing needs to be underlined, the set up preparation in order to run the experiment is a long process. It can take more than an entire day of work to prepare everything, assemble the pieces, seal the set up and run the experiment. The set up preparation requires 5 main procedures:

1. Co-OEC electro-deposition
2. MoS2 drop-casting
3. Ion transfer membrane preparation
4. CO2 saturation of the electrolizer
5. Set-up assembly and sealing

6.4 Set-Up Preparation Procedures

Set up preparation is far the most important and time consuming aspect of this work. It can take more than entire day of work to prepare every component, assemble the pieces, seal the set up and run the experiment. The set up preparation requires 5 main procedures that are required to run a wide range of experiments.

6.4.1 Co-OEC Electro-Deposition

Cobalt nitrate hexahydrate Co(NO3)2•6H2O 99.999% was purchased from Aldrich and used as received. Deposition of Co–Pi films (Co-OEC) on FTO was carried out in solutions containing 0.5 mM Co(NO3)2•6H2O and 0.1 M potassium phosphate (KPi) at pH 7.0 using a standard 3-electrode configuration comprising an FTO working electrode, a Pt counter electrode, and a Ag/AgCl reference electrode. The working electrode area which wasn’t supposed to be coated, the stainless steel side, was masked using scotch tape. Bulk electrolyses were performed in a two-compartment electrochemical cell with a glass frit junction of fine porosity. For catalyst electrodeposition, the auxiliary side held KPi electrolyte and the working side held KPi electrolyte containing 0.5 mM Co2+. Cobalt
solutions were prepared fresh for each experiment. The working electrode immersed in the solution was the a-Si-3jn piece from ITO-coated side. Pt mesh was used as the auxiliary electrode. Electrolysis was carried out between 1.30 and 1.35 V, according to the size of the surface to coat without stirring and without iR compensation and with the reference electrode placed a few mm from the ITO surface.

6.4.2 MoS2 Drop-Casting

MoS2 nanoparticles were purchased from Aldrich and used as received. After preparing a 2M solution in IPA and sintered for at least 20 min the solution can be used in drop casting.

Using drop cast few layers of MoS2 are deposited on the cathode side of the artificial leaf (stainless steel side) and let it dry until all the IPA evaporates. This procedure is repeated few times until the area to coat is fully covered of a layer of few micrometers of MoS2.
6.4.3 **Ion Transfer Membrane Preparation**

We use a Nafion proton permeable membrane and the preparation process consists of 5 steps:
1. Place the Nafion in a 5% hydrogen peroxide solution and heat the system to 80°C and soak it for 1 hour.
2. Rinse with DI water and soak it in a DI water at 80°C for 1 hour.
3. Soak the Nafion membrane in 0.5 M H2SO4 for 1 hour at 80°C.
4. Rinse with DI water and soak it in a DI water at 80°C for 1 hour.
5. Store the membrane in DI water.

This process lasts approximatively 5 hours and, in order to use the membrane, the preparation has to always stay wet.

6.4.4 CO2 Saturation of the Electrolizer

In order to saturate the electrolyzer with CO2 it is necessary to bobble CO2 inside the solution. The solution, usually 50% in volume of IL and water, is continuously mixed by a rotating magnet while CO2 is bobbled, usually 45 min for each 50 mL of solution.

6.4.5 Set-Up Assembly and Sealing

The assembly and sealing of the set up requires multiple steps because the coatings, the paints and the silicon glue has to dry before running the experiment. The first step is to
clean the pieces and especially the slides from extra silicon glue or previous coating. Pealing the extra material guarantees a smooth complete penetration of the slide into the body. After, if it is necessary for the pieces to be recoated with hydrophobic paint.

Figure 43. pre and after coating set-up

Once the slides are ready and dry it’s possible to insert the 3jn and the nation membrane in between using silicon glue and screws to seal them. While the silicon glue dries the Nafion membrane has to be kept wet so we use some wet cotton layer on the membrane while the rest is drying.
Once the slides are finally ready it’s possible to insert them into the body, pore the two electrolyzes in the set-up and seal everything with Silicon glue.
CHAPTER 7

EXPERIMENTAL CONCLUSIONS

In this chapter the discussion will include the new set-up used to perform the direct-photo-CO2 reduction, storing sun energy in the form of Syngas while CO2 is reduced, performing the solar-to-fuel transformation that we have discussed in the previous chapters.

7.1 Gas Chromatograph Analysis of H2 and CO Production

To verify the CO presence in the processed gases, after 30 minutes, a 1 mL sample was injected into the GC for detection showing a clear H2 peak visible at 1.8 min. of detection, as reported in (Figure 53). The CO peak was expected between 8 and 11 min, here we report our results.

In the interval where the CO peak was expected we registered some activities that can be considered CO but still is not a decisive result. We are trying to improve the set up and minimize the losses in order to have a result that is clear and unequivocal.
Concerning the CO peak, to the have a clear and fair understanding of the detected results, it has to be also added that having bigger peak areas for O2 and N2 with respect to CO and H2 does not reflect that the actual amount of air molecules was higher than the amount of syngas molecules.

Only after calibration of the Gas Chromatograph for the different gases will it be possible to judge the actual volume composition of the sample.
7.2 **Conclusions**

From the data already reported it can be certainly asserted that the results obtained with this double chamber co-catalyst system are promising but there is still another big step to do in order to make this system completely auto-sufficient.

7.2.1 **Next Step Analysis**

The current results are definitely not enough to claim to have found the final solution for the global energy problem but are definitely enough to consider this a hot topic and a good candidate for this purpose. Considering the time and the resources spent so far it can be said that this project needs more work to make the results more consistent, the system more efficient and reliable but, without doubt, this work has opened a new perspective on how to perform a solar-to-fuel CO2 reduction and a new approach to the photocatalysis in this field.

The main areas for improvement are:

- **MoS2 structure and deposition process.** The MoS2 bulk structure could be substituted with a monolayer or double layer photoactive structure allowing photo-activity also on the other side. plus, the drop casting deposition process is good in the short term experiments but do
not last long, the catalyst progressively detracts from the substrate during the experiment decreasing the efficiency of the system.

- **Ohmic contact between 3jn in series.** Putting two or 3 a-Si 3jn in series too many losses are reported due to the contact; progressively the series structure fails during the experiment. It’s important to find the best way to ensure that the potential produced by the system is the maximum possible. Knowing that one 3jn can produce at list 1.8 V we have to ensure that putting two or three in series will produce a potential as code as possible to 1.8x3 V because only in this way we can overcome the all the other losses of the system.

- **Characterization of the system performance and co-catalyst behavior.** We still haven't properly characterized the new system; it’s overall efficiency, its SFE, its catalyst combined system efficiency and its output flow. In order to scale up this system and have a clear and deep understanding of this new system and its real potential this analysis cannot be left behind.

### 7.2.2 Global Conclusions

Our planet’s current energy needs are now about 14 TW; we are going to need 16 TW by 2050 because there are going to be 6 billion new energy users. Nowadays one of
the main scientific discussions is about supplying the rising need for energy in an environmental friendly way.

Center of concern for the scientific community, once proved as the major cause of the ‘‘greenhouse effect,’’ CO2 reduction has become the common goal of both government and scientists. The idea that the emissions of this gas has to be minimized has been a major concern in the global debate and finding the ideal fuel, something that is suitable to satisfy the energy demand without releasing vast quantities of carbon dioxide in its production and in its consumption, is the key objective of vast number of research projects.

The only renewable and carbon-neutral energy source able to replace fossil fuels and meet rising global energy demand is Sunlight (120,000 TW)[12]. But it requires an efficient and cost-effective storage mechanism. Nature has given us the blueprint for storing sunlight in the form of chemical fuels, embedding sun energy in chemical bonds.

The aim of this project is to find a new to solution to the energy problem.

The integration of earth-abundant catalysts with photovoltaic multijunction cells captures the functional elements of energy capture and storage of a leaf. Following this idea I have produced a prototype that, by using only the Sun, is able to convert CO2 and water to produce CO, hydrogen (a well known fuel: syngas) and O2. Syngas is a combustible that can be easily recombined into a several other types of fuel (gasoline or methane). Furthermore burring H2 or Syngas like a classic internal combustion engine’s
fuel is not the only option: recombine Hydrogen with Oxygen will “greenly produce” clean water and electricity.

This possibility discovers new scenario where the Sun drives high energy reaction directly, with no use of wires, under a simply engineered configuration. For example, the previously described design can be readapted from a PV configuration to a “standalone” device with (nano)particles in solution[1]. Moreover, solving a few minor issues like the protection of the artificial leaf from acidic media plus increasing the light absorption and conversion efficiency could transform it in the more effective way to store and reconver solar energy.

7.3 Future Evolutions

The device has a structure fairly close to the one of PV panels and its usage could be close too; it could be used both for intensive industrial energy production and for “in loco” energy supply. The prototype still needs development especially for scaling up it’s production rate but it’s easy to manufacture, easy to use and maintain and it’s very versatile. So I think that a front investment (I don’t know how much but according to other similar start-up between $3 and $5 million) is necessary to finalize it and start the production and distribution of the device. A second phase could lead to an intensive production green plant where the solar-to-fuel can be coupled with a waste-incinerator and
a water-purification plant. The waste incinerator will provide CO2 reusing waste, the solar-to-fuel power plant will use it to produce syngas and more devices while it will work as a water purification and electric production power plant too: takes-in water (ex river) use it in its processes and gives back clean water and electricity though fuel-cell reaction.
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