IOP Conference Series: Earth and Environmental Science

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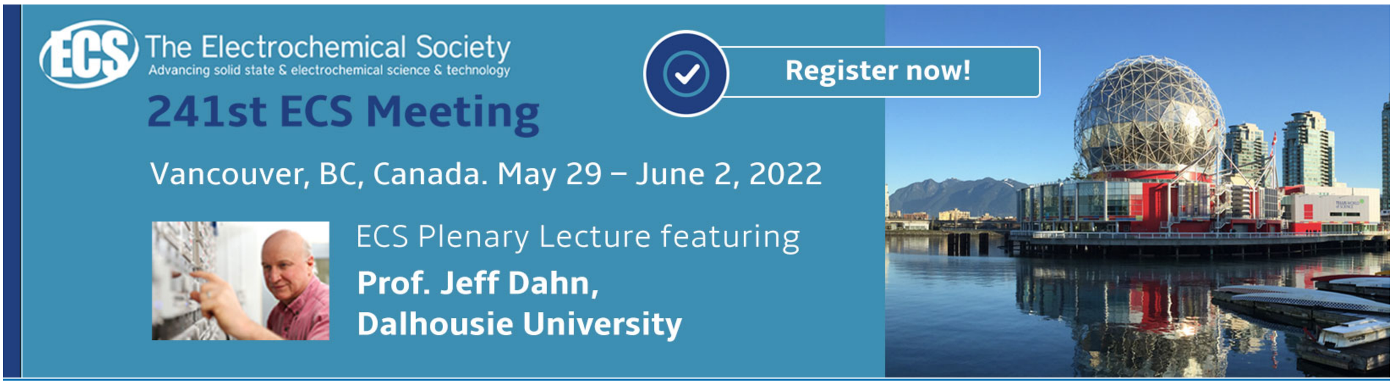
To cite this article: Houda Ennaceri and Bernd Abel 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **291** 012038



Conversion of carbon dioxide into storable solar fuels using solar energy

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Abstract. Nowadays, there are two main energy and environmental concerns, the first is the risk of running out of fossil fuels in the next few decades, and the second is the alarming increase in the carbon dioxide concentrations in the atmosphere, causing global warming and rise of see levels. Therefore, solar-driven technologies represent a substantial solution to fossil fuels dependence, global warming and climate change. Unlike most scientific research, which aim to use solar energy to generate electricity, solar energy can also be harnessed by recycling the carbon dioxide in the atmosphere through high-tech artificial photosynthesis with the objective of producing storable and liquid solar fuels from CO_2 and water. There are two types of solar fuels, the first being hydrogen, which can be produced by mean of water splitting processes. The combustion of hydrogen generates water, which is a completely clean option for the environment. The second type of solar fuels consists of carbon-based fuels, such as methane (CH_4), carbon monoxide (CO), or alcohols such as methanol (CH_3OH) and ethanol (C_2H_5OH). The production to liquid solar fuels liquid fuels is of great interest, since they can be used in the current industrial infrastructures such as the automobiles' sector, without substantial changes in the vehicles' internal combustion engines. Therefore, guaranteeing a smooth transition from fossil fuel energy to renewable energy without radical economic consequences. Also, and most importantly, when these solar fuels are burned, they will only release the exact amount of CO_2 which was initially used, which represents an optimal process for sustainable transport.

1. Introduction

Today, the main energy concern is running out of conventional fossil fuels, which is the reason behind shifting towards renewable energies. The population growth and the aggressive consumption of energy are leading to alarming depletion of fossil fuels such as oil and gas, as well as increasing levels of pollution [1]. In fact, according to the united nation population division, the world population has reached 7 billion in 2011, and is projected to reach more than 9 billion by 2050, which will drastically increase the energy demand. According to Hubbert peak theory, there will be an extreme drop in oil resources within the next 40 years [2, 3]. Therefore, years between 2055 and 2060 will possibly be the time when the oil production will reach zero. Moreover, and considering the current energy consumption rate, the World coal institute's estimations expect that the current coal reserves will last for another 130 years, oil reserves for 42 years, and natural gas reserves for 60 years. The need to replace the traditional fossil fuels by sustainable options and new energy scenarios is therefore becoming very crucial. Another serious environmental concern is the increasing concentrations of carbon dioxide (CO_2) in the atmosphere, which is produced by burning fossil fuels and is responsible for global warming problems [4, 5]. In fact, the concentration of carbon dioxide in the atmosphere has severely increased from 280 ppm in 1750 to 400 ppm in 2014 [6]. The increase of the human-induced CO_2 has devastating consequences such as the increase of average temperatures, sea ice melting, floods and rise of sea levels, affecting the overall life, health and economy in the world. According to the Intergovernmental Panel on Climate Change (IPCC), the carbon dioxide atmospheric concentration has to be stabilized by reducing the 2006 global CO_2 emissions levels by 50% in 2050, by 100% in 2075, and above 100% by 2100 [7, 8]. Currently, the available technologies to tackle the CO_2 global warming problems is the sequestration process, also referred to as the carbon capturing and storing (CCS) process, which consist of capturing CO_2 at major outlets, compressing it in the form of a liquid for practical transportation, and storing it in underground sites or under deep sea levels [9]. Although CCS process can greatly reduce the CO_2 concentrations in the atmosphere, this procedure is extremely expensive and has different safety related uncertainties. In fact, the capital cost for a coal power plant using the CCS process is extremely higher compared to a conventional plant not equipped with CCS [10, 11]. A sustainable energy process is to produce energy from CO_2 instead of capturing and disposing it. In fact, CO_2 can be converted into value-added chemicals such as hydrogen, methanol and ethanol following some of the thermochemical routes. These fuels can be used to power cars without performing significant changes in their internal combustion engines, leading to a new route for sustainable future. In order to overcome today's drastic depletion of fossil fuels and mitigate the global warming risks related to the high concentrations of CO_2 in the atmosphere, finding sustainable options and new energy scenarios, mainly the conversion of CO_2 into value-added chemicals using sunlight is one of the top-most research priorities. In fact, the world's perception of carbon dioxide is recently changing, starting to consider CO_2 as a value-added gas, rather than a waste [12].

The purpose of our current work is the production of renewable solar fuels in liquid form such as methanol and ethanol from carbon dioxide and water. The production of solar fuels can be achieved by water splitting thermo-chemical reactions and carbon dioxide reduction under sunlight. This topic is nowadays considered one of the hottest research topics and top-most research priorities, which represents a sustainable energy source supply, and would a great impact on future energy options.

2. Background and rationale

The production of solar fuels can be achieved through artificial photosynthesis process [13, 14], which is similar to the natural photosynthesis, where green plants use the sunlight to convert water and carbon dioxide into oxygen and hydrocarbons according to the following reaction:

$$6CO_2 + H_2O \xrightarrow{light\ energy} C_6H_{12}O_6 + 6O_2 \tag{1}$$

Theoretically, the conversion efficiency of artificial photosynthesis is proven to be much higher compared to its naturally occurring counterpart. It fact, natural photosynthesis of plants do not exceed 1% conversion efficiency [15], while the artificial photosynthesis is expected to reach more than 40% conversion efficiency, which is similar to the theoretical efficiency of tandem solar cells. The artificial photosynthesis can be achieved by the use of strong catalyst materials to produce liquid solar fuels or fuel precursors such as carbon monoxide (CO) and solar hydrogen (H_2). These two fuel precursors are referred to as synthesis gas or syngas. One of the main issues regarding the CO_2 reduction to liquid fuels is the assemblage of nuclei and formation of chemicals bonds, which would allow the reduction of CO_2 molecule into more complex molecules. This can be achieved using two different methods, the first by converting CO_2 and H_2O into synthesis gas (CO and H_2), and then convert the synthesis gas into liquid fuels such as gasoline using the Fischer-Tropsch process according to Equation (2), where n is an integer, with values ranging from 10 and 20:

$$(2n+1)H_2 + n\,CO \rightarrow C_nH_{2n+2} \tag{2}$$

The second method is to attempt to produce CO_2 directly to liquid fuels through photo-catalytic or electro-catalytic processes. The first method is substantially easier to achieve since it is easy to convert carbon dioxide (CO_2) to carbon monoxide (CO), and to convert water (H_2O) to hydrogen (H_2). The second method is, on the other hand, more perplex since it involves ore kinetic challenges [16]. The key success of converting CO_2 directly to liquid fuels resides in identifying a strong catalyst which can do the complete sequence of converting CO_2 into hydrocarbons or alcohols with low kinetic barriers. The principle of artificial photosynthesis consists of sunlight absorption by a semiconducting material and the excitation energy creates an electron-hole pair. Before the photo-excited electrons ($e-$) and holes ($h+$) recombine, the holes oxides water on the catalyst's surface and provide protons for the CO_2 reduction process as shown in equations (3) to (5) [17]:

$$H_2O + h^+ \rightarrow OH^{\cdot} + H^+ \tag{3}$$

$$H_2O + 2h^+ \rightarrow H_2O_2 + 2H^+ \tag{4}$$

$$2H_2O + 2h^+ \rightarrow 4H^+ + O_2 \tag{5}$$

The electron transfer from the conduction band produces carbon dioxide anion radicals ($\cdot CO_2^-$) and hydrogen radicals ($\cdot H$) through the following equations:

$$H^+ + e^- \rightarrow \cdot H \tag{6}$$

$$CO_2 + e^- \rightarrow \cdot CO_2^- \tag{7}$$

These radicals form other stable hydrocarbons such as methane (CH_4), methanol (CH_3OH), carbon monoxide (CO), formic acid ($HCOOH$), formaldehyde ($HCHO$), or ethanol (C_2H_5OH) as shown in equations (8) to (13) [17]:

$$\cdot CO_2^- + 8 \cdot H + 8h^+ \rightarrow CH_4 + 2H_2O \tag{8}$$

$$\cdot CO_2^- + 6 \cdot H + 6h^+ \rightarrow CH_3OH + H_2O \tag{9}$$

$$\cdot CO_2^- + 2 \cdot H + 2h^+ \rightarrow CO + H_2O \tag{10}$$

$$\cdot CO_2^- + 2 \cdot H + 2h^+ \rightarrow HCOOH \tag{11}$$

$$\cdot CO_2^- + 4 \cdot H + 4h^+ \rightarrow HCHO + H_20 \tag{12}$$

$$\cdot CO_2^- + 12 \cdot H + 2h^+ \rightarrow C_2H_5OH + 3H_2O \tag{13}$$

One of the major considerations of semiconductor photocatalysis is the recombination of the photo-generated electron-hole pairs, which reduces the overall quantum efficiency [18]. The lifetime of the photo-generated electron-hole pairs is only some few nanoseconds, which is suitable for stimulating redox reactions. The reduction of CO_2 is more challenging compared to water splitting. In fact, the production of hydrocarbon fuels requires multi-electron processes, transfer of electrons and protons, and breaking the C-O bonds to create new C-H bonds [17].

The artificial photosynthesis reduction of CO_2 depends on the following central factors [19]:

- The high reduction potential of a single electron (Equation (7)): (E0 = - 1.9 V versus the normal hydrogen electrode (NHE))
- The solubility of carbon dioxide (CO_2) in water
- The competition of hydrogen formation.

In order to overcome these limitations, the choice of the candidate catalysts and the reaction conditions and parameters such as the reductants, light intensity, temperature, and pressure need to be optimized. Different metal oxides have been tested in the literature to achieve carbon dioxide thermochemical dissociation or splitting such as zinc oxide [20], titanium dioxide [21], graphene [22] and ferrites [23]. Zinc oxide and ferrite have been proven not to be good candidates for solar fuel production as zinc oxide presents volatility and quenching problems [24], and ferrites present slow kinetics [25]. Ceria

(CeO_2) has also been used for CO_2 splitting and production of solar fuels because of its high melting point and high catalytic activity for CO_2 reduction [26]. However, cerium-based catalysts have been shown to get easily deactivated by a small coverage of deposited carbon [27]. Generally, in order to achieve CO_2 reduction and water oxidation using semiconductor photo-catalysis, the position of the valence band of and conduction band of the semiconductor photo-catalyst should match the oxidation and reduction potentials of water splitting and CO_2 reduction.

3. Methods

Ethanol and methanol have high energy densities of 20.9 MJ/L and 15.6 MJ/L, respectively, compared to gasoline which has an energy density of 34.2 MJ/L [28]. Ethanol and methanol can be used in fuel cells to produce electricity, or can be directly used as alternative fuel for internal combustion in the automobiles' sector. The advantages of producing these fuels from CO_2 reside in their low toxicity, safety to handle, and the possibility to be used as car fuels without modifications in their internal combustion (IC) engines. Also, these liquid fuels do not need high pressure to be stored at room temperature. The CO_2 molecule has a high kinetic stability. Therefore, efficient catalysts are needed for a successful CO_2 hydrogenation, which is the main objective of my research.

The electrochemical reduction of CO_2 into liquid solar fuels such as methanol and ethanol requires complex multi-electron processes. In fact, the CO_2 electrochemical reduction to methanol requires 6 electrons/protons, and the CO_2 electrochemical reduction to ethanol requires 12 electrons/protons. In order to assess the catalyst's performance towards CO_2 reduction, different parameters need to be investigated such as:

- The overpotential, which is the difference between the standard thermodynamic redox potential, and the actual onset potential at which the reduction is experimentally occurring.
- The current density, which is the current divided by the geometric surface area of the working electrode
- The faradaic efficiency of each reduction product ($\alpha * n * F/Q$), where α is the number of electrons transferred, n is the number of moles of a specific product, F is Faraday's constant (96485 C mol^{-1}), and Q is the charge that is passed through the electrolysis process ($I*t$)
- The energetic efficiency ($E_0 * FE/V_{in}$), where E_0 and FE are the standard potential and the faradaic efficiency of the reduction product, respectively, and V_{in} is the total cell voltage
- Turnover number (TON), which is the number of moles of the formed product divided by the number of active centers.
- The Tafel slope, which relates the overpotential to the logarithm of the partial current density of the product.

4. Summary

Different metal electrodes are electrochemically active towards CO_2 reduction and can be divided in 3 groups. The first group (e.g. Sn, Hg, In, Pb, Cd, Bi) produces formic acid or formate as reduction products. On the other hand, the second group of metals (e.g. Au, Ag, Pd, Zn, Ga) generates gaseous carbon monoxide as reaction product. The last group is composed of copper only, which has been shown to be the most promising metal in the electrochemical CO_2 reduction since it is the only metal catalyst that can electrochemically convert carbon dioxide into oxygenates/hydrocarbons. However, the main drawback of using copper and copper-based catalysts is their long-term stability.

Special attention is given to the development of efficient catalysts for the (photo) electrochemical reduction of CO_2. In fact, a suitable semiconductor photo-cathode should have a high absorption in the visible range, high stability, high photo-potential efficiency, low kinetic over-potentials and good charge transport. Therefore, in order establish and scale-up a technology for solar fuel production, it is essential to develop and design new functional, low-cost, durable, highly stable and energy-efficient thin films used as photo-cathodes.

The photo-cathode performance is also sensitive to the deposition method. Hence, optimizing and controlling the film thickness, morphology, and crystal structure is of great interest. Moreover, and as explained earlier, the production of hydrocarbon fuels requires multi-electron processes, transfer of electrons and protons, and breaking the C-O bonds to create new C-H bonds. Therefore, a complete characterization of the molecular, electronic, and nuclear structure of the tested materials is very crucial to understand the bonding interactions and the chemical reactivity.

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Acknowledgments

The funding to conduct this work has been provided by the Alexander von Humboldt Foundation.