Electrocatalytic CO2 reduction toward liquid fuels : on heterogeneous electrocatalysts and heterogenized molecular catalysts

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Citation

Birdja, Y. Y. (2018, April 19). *Electrocatalytic CO2 reduction toward liquid fuels : on heterogeneous electrocatalysts and heterogenized molecular catalysts*. Retrieved from https://hdl.handle.net/1887/61513

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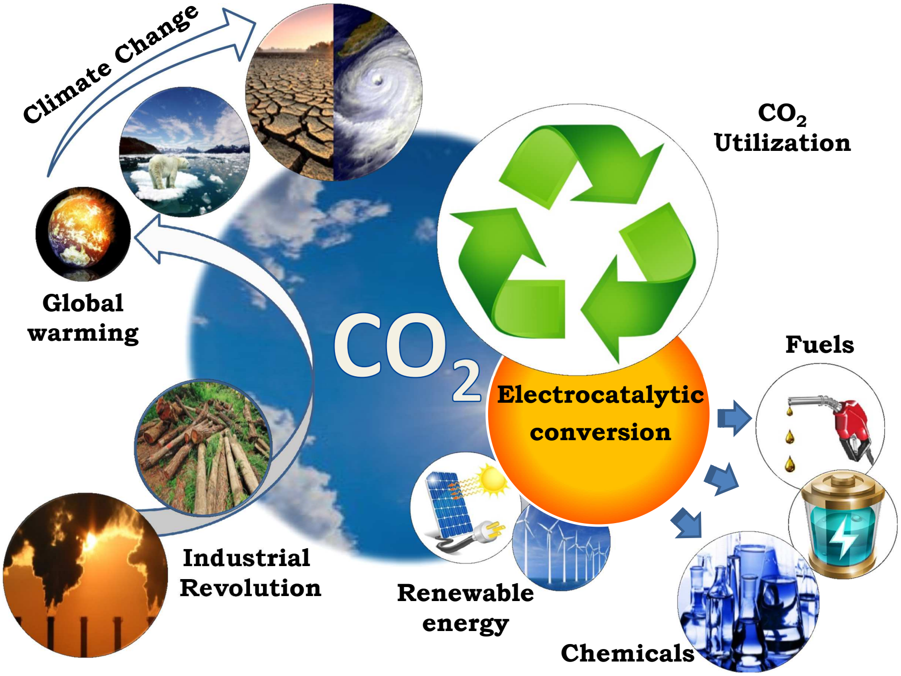
Date: 2018-04-19

CHAPTER 1

General Introduction



1.1 The *status quo* of the global carbon cycle

The earth is the only planet known to date that can sustain life. The ability to make life possible, is related to the composition of the Earth's atmosphere, which enables a relatively constant temperature. The gases responsible for maintaining this temperature are the so-called greenhouse gases (e.g. water vapor, carbon dioxide, methane and nitrous oxide). The concentration of greenhouse gases (GHGs) are influenced by the interplay of (a)biotic processes on Earth, which are represented by global biogeochemical cycles of the related elements. The scope of this thesis is associated with the carbon cycle (Figure 1.1), which consists of smaller cycles with different time scales, wherein carbon is exchanged between the atmosphere, lithosphere, hydrosphere and biosphere by several processes of which photosynthesis is the most important natural process for living organisms.[1]

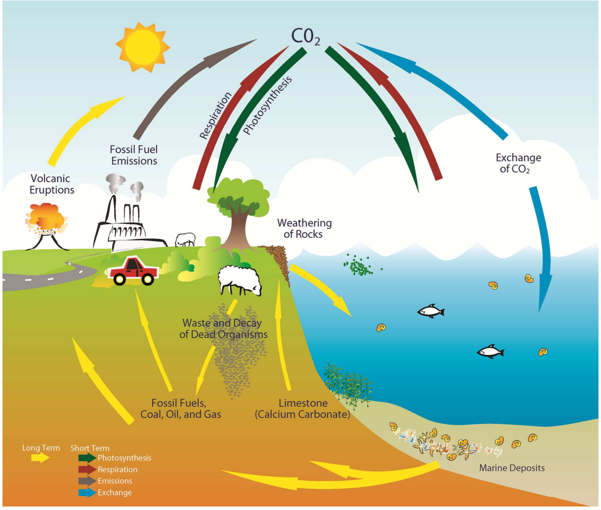


Figure 1.1 Schematic representation of the carbon cycle.[2]

Starting from the Industrial Era around 1750, the carbon cycle has been perturbed significantly by human activities such as fossil fuel combustion, industrial processes and deforestation, leading to substantial emission of CO_2 in the atmosphere. Atmospheric CO_2 levels have increased from 278 ppm to 390.5 ppm in the timespan of 1750 - 2011, with an alarming rate of 2.0 ± 0.1 ppm/year during 2002 - 2011.[3] To reach the target set by *The International Energy Agency* of $<$ 2° rise in global temperature by 2050, CO_2 emissions should be reduced by at least 50 % compared to 2011.[4] Other factors such as the higher energy demand of mankind and their fossil fuel dependence, the economic growth and the increase in world population indirectly contribute to this anthropogenic CO_2 accumulation in the atmosphere. Consequences of these influences to the carbon cycle are: global warming, climate change, acidification of oceans, increased seawater levels, etc.[5] Climate change is even envisaged to be one of the most challenging problems of the 21st century.[6] Not entirely coincidental, at the time of writing this section, the record of warmest October day in the Netherlands since the start of the temperature measurements in 1901, has been broken.[7]

1.2 Anthropogenic CO_2 emissions; *quo vadis?*

Over the past few decades, much attention has been given to the mitigation of GHG emissions, and various political policies have covered these topics, aimed at reducing climate change (e.g. Montreal protocol, Kyoto protocol, Copenhagen Accord, Paris agreement).[8] Several strategies have been proposed to remove CO_2 from the atmosphere, or to alleviate anthropogenic CO_2 emissions.

Utilization of CO_2 is preferred above carbon storage methods, since CO_2 can be used as sustainable feedstock for other processes, which simultaneously addresses important issues such as the sustainable energy production, increasing world population, food production, etc.[9,10] CO_2 utilization can be carried out without CO_2 conversion such as in enhanced oil recovery applications, or with conversion of CO_2 by means of thermal, chemical, biological, electrochemical, and photochemical methods.[6,11,12]

In order to curb the CO_2 emissions, decarbonization of the energy system is required. Furthermore, the electricity sector is projected to undergo a transition toward renewable sources, where solar power is likely to become the dominant energy source by 2050.[4] Several researchers proposed solar energy utilization as a key route to meet the targets for 2050 regarding anthropogenic CO_2 mitigation and climate change.[6,13] In a process similar to photosynthesis, we are able to use sunlight and a catalyst to store solar energy in chemical bonds. In this respect, the electrochemical conversion of CO_2 is very attractive for the production of so-called ”solar fuels”. In this thesis we elaborate on the electrochemical CO_2 conversion toward ”electrofuels”, which is the broader term used when electricity from different renewable sources are stored in chemical bonds. This process has been shown to be very promising as its effects are multi-fold, *viz.* reduction of CO_2 emissions, production of commodity chemicals, and storage of renewable energy in fuels, which is important due to the intermittent character of renewable energy sources (e.g. solar- and wind energy).[14]

1.3 Electrocatalytic conversion of Carbon Dioxide toward Electrofuels

Carbon dioxide is the most stable form of carbon, and therefore abundantly present in the atmosphere. Conversion of CO_2 is an endothermic process, and a catalyst is needed to obtain reasonable rates of conversion. Electrocatalytic conversion of CO_2 and electrocatalysis in general have several advantages: we are able to control the reaction by the applied potential, use water as proton donor, and work under ambient conditions.[15] Bottlenecks are the high overpotentials, the broad product spectrum, and competitive hydrogen evolution (in aqueous media), which are thoroughly discussed and reviewed by many researchers in the field.[6,14,16,17] An extended discussion about the recent advances and challenges in the electrocatalytic reduction of CO_2 is given in chapter 2.

Depending on the electrocatalyst, different products can be formed, which leads to a selectivity issue.[16,18,19] Several electrofuels have been discussed in the past for a sustainable society (e.g. the hydrogen economy and methanol economy).[20–22] Although many of the products from CO_2 reduction can be used for further processing, from a renewable energy perspective, the formation of liquid products is preferred, since the existing energy infrastructure is based on liquid fuels. Additionally, liquid products such as formic acid, methanol and ethanol can be employed directly in fuel cells.

Except for formic acid, the formation of liquid products which are higher electron transfer products from electrocatalytic CO_2 reduction, is generally more complex compared to the production of 2-electron transfer products, and the electrocatalyst is more difficult to optimize.[23] We still lack significant mechanistic insight in these electrochemical processes in order to improve the electrocatalytic CO_2 reduction performance. These are the main reasons for the increasing research activity on the topic of electrocatalytic CO_2 reduction toward liquid products, to which the work described in this thesis is devoted.

1.4 Outline of this thesis

The focus throughout this thesis will be on the electrocatalytic reduction of carbon dioxide in aqueous media toward liquid products. The thesis can be divided in two parts. The first part (chapters 2 and 3) is about heterogeneous electrocatalysis of CO_2 reduction, and the second part (chapters 4 - 7) concerns electroreduction of CO_2 on heterogenized molecular catalysts.

In chapter 2, we review the recent advances and challenges in the field of electrocatalytic CO_2 reduction mainly on heterogeneous catalysts. Important topics will be highlighted and discussed such as initial activation of CO_2, the influence of reaction- and process conditions, the electrode morphology, and carbon-carbon bond formation. Moreover, we will discuss two important techniques often used in CO_2 electroreduction research: in situ spectroelectrochemical techniques and computational approaches for CO_2 reduction. This chapter will be concluded with our perspectives for future research of electrochemical CO_2 reduction.

Chapter 3 presents the crucial importance of the effect of local pH changes during CO_2 reduction on the product distribution. We demonstrate the involvement of disproportionation reactions leading to product distributions which should be distinguished from direct CO_2 reduction. These reactions are promoted by the local pH (changes) during CO_2 reduction, as a result of the simultaneous hydrogen evolution reaction. The importance of this phenomenon is illustrated by generalizing to other reactants and to different electrode materials.

The remaining chapters are related to molecular catalysts, which we introduce with a brief review into the field of molecular catalysis of CO_2 reduction in chapter 4. Moreover, we give an overview of catalysts and recent developments related to heterogenized (molecular) catalysts, with special attention to metalloporphyrins, which are the catalysts under study in the remainder of this thesis.

In chapter 5, we report on the influence of the metal center of immobilized metalloprotoporphyrins on the electrocatalytic CO_2 reduction toward formic acid. We show that rhodium, tin, and indium metal centers are active for formic acid production in the order Rh < Sn < In. We discuss the coupling with the hydrogen evolution reaction, which plays an important role for the selectivity toward formic acid. Additionally, we demonstrate that the faradaic efficiency toward formic acid is strongly dependent on the bulk pH of the electrolyte and applied potential.

In chapter 6, we build upon the findings obtained in the previous chapter, by studying the immobilized indium(III) protoporphyrin for CO_2 electroreduction toward formic acid in more detail. We show the significant influence of the nature of the substrate on the selectivity, reactivity, and stability of CO_2 reduction toward formic acid. Moreover, we study the influence of the surface chemical functionality, and catalyst's chemical environment by respectively electrochemical and plasma treatment of the substrate, and by immobilization of the indium(III) protoporphyrin in polymer membranes. The findings in this work allow for design and optimization of heterogenized molecular systems for CO_2 electroreduction beyond empirical considerations.

We continue with the investigation of immobilized indium protoporphyrin catalyst in chapter 7. Herein we optimize CO_2 reduction performance by modification of the electrolyte composition. We demonstrate the impact of the electrolyte and the buffer strength on the selectivity and activity of CO_2 reduction. Moreover, we discuss factors affecting the stability of the system.

1.5 References

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