



Universiteit  
Leiden  
The Netherlands

## **Electroreduction of nitrate and carbon dioxide on copper electrodes: a mechanistic study**

Perez Gallent, E.

### **Citation**

Perez Gallent, E. (2018, February 1). *Electroreduction of nitrate and carbon dioxide on copper electrodes: a mechanistic study*. Retrieved from <https://hdl.handle.net/1887/61142>

Version: Not Applicable (or Unknown)

License: [Licence agreement concerning inclusion of doctoral thesis in the Institutional Repository of the University of Leiden](#)

Downloaded from: <https://hdl.handle.net/1887/61142>

**Note:** To cite this publication please use the final published version (if applicable).

Cover Page



Universiteit Leiden



The following handle holds various files of this Leiden University dissertation:

<http://hdl.handle.net/1887/61142>

**Author:** Perez Gallant, E.

**Title:** Electroreduction of nitrate and carbon dioxide on copper electrodes: a mechanistic study

**Issue Date:** 2018-02-01

# **Chapter 1**

## **Introduction**

## 1.1 The Birth of Electrochemistry

Despite the broad knowledge of electricity gained during the 17<sup>th</sup> and the 18<sup>th</sup> century by scientists like William Gilbert, Stephen Gray, Charles Francois, Jean-Antoine Nollet, William Watson and Charles-Augustin Coulomb, among others, it was not until the late 18<sup>th</sup> century that Luigi Galvani pronounced the birth of electrochemistry by creating a bridge between muscular contractions of a frog's leg and electricity. In 1791 Galvani established that animals hold a vital force, namely "animal electricity", which activates muscles when placed between two metals. Alessandro Volta postulated that the real source of stimulation was the contact of dissimilar metals connected by a moist conductor (a frog's leg). Volta persistently studied this phenomenon in order to explain his "contact" theory of electricity, and in 1800 he announced his invention of the first electrical battery, the voltaic pile. Years later, Humphry Davy established that the voltaic pile produces electricity depending on the event of chemical reactions, and not just on the contact of dissimilar metals as Volta proposed. Davy's successor, Michael Faraday, studied the effects in electrochemical decomposition, which was discovered by Paets van Troostwijk and Deiman by splitting water into hydrogen and oxygen by electrolysis. Faraday concluded that the passage of electricity through a conducting liquid medium causes the molecules to dissociate and the amount of product decomposed was directly proportional to the amount of electricity passing through the solution. These laws are still fundamental to industrial electrolytic production of chemicals. This story illustrates how even an immature, undeveloped or imperfect scientific idea can assist in the development of a cultivated and world-wide accepted scientific theory. Every minor stage in research triggers the commence of an open discussion that with effort, time and lots of re-thinking and understanding will result in a putative theory.

## 1.2 Electrocatalysis

A catalyst is defined as a substance that intervenes in a chemical reaction modifying the reaction rate without being consumed or chemically changed. Electrocatalysts are specific forms of catalysts where the rate of an electrochemical reaction occurring on an electrode surface is enhanced. Electrocatalysts are classified in two categories: homogeneous, in which catalyst and reactants have the same phase, and heterogeneous, where the reaction takes place at the interface between the catalyst (the electrode) and the reactant phase. In electrocatalysis, the reactions involve electric charges flowing between the electrodes and the ionic conductor, the electrolyte. Thus, electrochemistry handles the interaction between electrical energy and chemical change.

Every electrochemical cell reaction consists of two half reactions, one occurring at the anode where a certain substance will donate electrons and become oxidized, and one occurring at the cathode where a certain substance will accept electrons and become reduced. This thesis is focused on reduction reactions of nitrate and carbon dioxide taking place at a cathode made of a solid metal electrode, mainly copper.

The performance of the catalyst for a certain reaction depends on a vast number of parameters, such as electrode material, oxidation state of the material, electrode morphology, surface roughness, differences in adsorption sites, pH and the nature of the species in solution, etc. A good strategy to develop an active and efficient new catalyst is by first determining how all these parameters affect the reaction and its mechanism. In that vein, the scope of this thesis is to investigate the mechanism of nitrate and CO<sub>2</sub> reduction and how different parameters have an impact on the catalytic performance of copper.

### **1.3 The potential of electrochemistry in industrial processes**

The use of electrochemical techniques for the synthesis of valuable products provides several advantages over chemical synthesis. An important advantage that makes electrochemistry attractive for industry is the ease of scalability, which allows large-scale chemical production. A classic example of ton-scale production is the chloralkali process<sup>2</sup>, where aqueous sodium chloride, normally brine obtained directly from natural salt deposits, is electrolyzed to form chlorine gas and sodium hydroxide. The chloralkali process is the largest of the electrolytic industry. The preparation of chlorine electrochemically in industrial scale was first achieved in 1892. In 1987 it was responsible for about 10% of the total world production, and in 2000, 95 % of the world's chlorine production was obtained by the chloralkali process<sup>3</sup>. Another example of large-scale synthesis is the Hall-Héroult process, where  $\text{Al}_2\text{O}_3$  is electrolyzed to produce elemental aluminium<sup>4</sup>. The Hall-Héroult process is the largest in terms of energy usage in industrial processes<sup>5</sup>. In addition, organic chemicals such as adiponitrile, an intermediate to nylon, or ethylene glycol, used as antifreeze or in PET bottles, are also produced electrochemically in large scale. 200 million kg of Adiponitrile are produced per year by electrohydrodimerization of acrylonitrile<sup>6</sup>, and about 10 billion kg of ethylene glycol are produced per year by catalytic oxidation of ethylene oxide followed by hydrolysis<sup>5</sup>.

One of the most important contemporary benefits of electrochemistry in industrial processes is an environmentally friendly and clean process by employing renewable electricity. Electrochemical processes use electric current as energy source, averting the use of stoichiometric amounts of oxidants or reductants, dramatically lowering the amount of by-products formed and thus the pollutant levels. A precise control of oxidation or reduction levels can be achieved by the adjustment of the electrode potential. The electrochemical synthesis of compounds offers a precise control of the product yield through the applied current or

potential, virtually leading to higher energy efficiencies compared to thermal-based processes, and to more pure products than those synthesized by chemical routes. The electrochemical synthesis of DZ-2384, a diazoamide-based preclinical candidate for oncology, marked an improvement in terms of selectivity and environmental footprint. This substance is now prepared by an intramolecular electrochemical oxidative coupling<sup>7</sup>, while previously it was synthesized with the use of oxidants such as  $\text{PhI}(\text{OAc})_2$ . The reagent-based process led to significant by-product formation which limited the yield of DZ-2384 and complicated its purification<sup>7-9</sup>.

The use of less extreme process conditions such as lower temperature and pressure potentially leads to less degradation of the starting material or products, making electrochemical methods industrially interesting. In addition, a lower number of steps might be involved in the process, for instance, by combining in one reactor the electrochemical synthesis and the product separation. In the chloralkali process, the formation of chlorine gas occurs in the anodic compartment of the reactor, whereas sodium hydroxide is formed in the cathodic compartment; therefore, the separation process is direct.

However, the existence of physical restrictions such as mass transport limitations and more importantly economically unprofitable processes, makes electrochemical processes less beneficial. For large-scale production, electrochemical processes are costly. The traditional chemical preparation, even being less selective, is usually economically more beneficial<sup>5</sup>.

Electrochemical routes are not always economically feasible if the selectivity for the desired product is low or inadequate. In aqueous systems where the competitive reaction is based upon oxygen or hydrogen formation, the process becomes especially unfeasible in economic terms, due to the ease of  $\text{H}_2$  or  $\text{O}_2$  production compared to the formation of the desired product. In electrochemical processes, high-energy consumption is usually required.

However, direct conversion with the use of renewable energies offers a cheap source of energy which may partially help overcome this problem. In addition, the use of abundant and thereby less expensive starting materials such as CO<sub>2</sub> and nitrate also helps in counteracting the expenses and readjusting the balance to beneficial values.

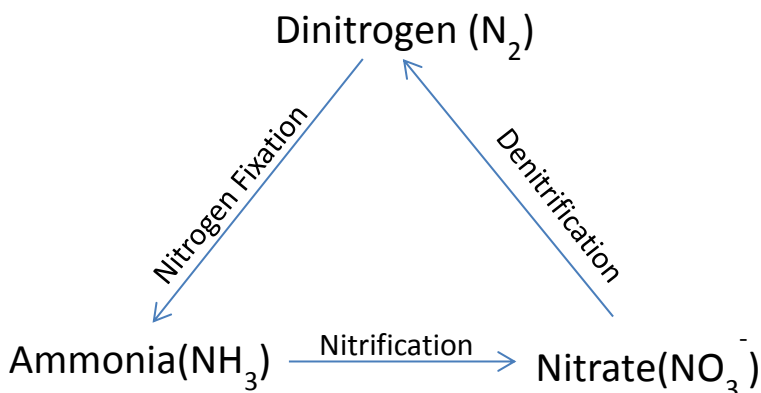
Despite the advantages previously mentioned, it is important to remark the existence of several drawbacks which limit the industrial application of electrochemical processes. Important factors that make processes economically unfeasible are the short lifetime and/or the high cost of some electrode materials. Ideally, the electrode material should be cheap and stable in the electrolysis medium. In addition, some electrochemical reactions have low current efficiency under some conditions and/or high activity towards side reactions limiting the production yield of the desired product. It is important to mention the vast amount of factors that affect electrochemical conversion and, therefore, determine the electrolysis performance<sup>10</sup> such as the electrolyte nature, concentration, pH or conductivity and the nature and structure of the catalyst, among many others. Other factors such as the potential or current distribution, the mass-transport regime and the electrochemical cell design are also of paramount importance<sup>11</sup>. The geometry of the electrodes, the inter-electrode distance, the cell dimensions and the operation mode of the reactor, among others, are decisive parameters that affect the electrochemical performance of the process<sup>10</sup>.

In the interest of eventually obtaining an efficient and economically feasible process for the industry, a detailed mechanistic study of the reaction must be addressed, to understand which factors play a role in the efficient and selective formation of the desired product. An attractive process would be the conversion of a cheap and abundant substance to a more valuable product. In this thesis three different reactions and their mechanisms are the object of study: the electrocatalytic reduction of nitrates to hydroxylamine, and the electrocatalytic reduction of carbon dioxide for two different purposes,

namely the formation of hydrocarbons and the formation of cyclic carbonates.

## **1.4 Electrocatalytic reduction of nitrate**

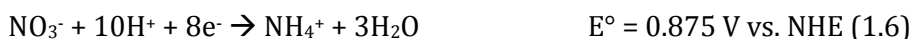
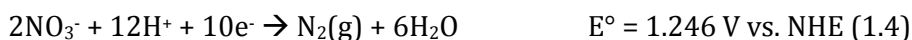
The reduction of nitrate has attracted interest due to its environmental significance<sup>12</sup> in view of the contamination of groundwater,<sup>13-14</sup> and because it causes serious health problems<sup>15</sup> such as liver disease, cancer and blue baby syndrome. Nitrate contamination is a result of industrial waste, nuclear industries and agricultural runoff such as livestock feces and the use of fertilizers, which currently induce severe alterations in the nitrogen cycle<sup>16</sup>. This biogeochemical cycle is a complex network of biological and abiotic processes through which nitrogen circulates through the organic and physical world. A very simplified scheme of the nitrogen cycle is displayed in Fig.1.1. The atmosphere is the main reserve of nitrogen, however, the majority of the living beings cannot use atmospheric nitrogen to generate amino acids and other nitrogen-based compounds. Therefore, atmospheric nitrogen must be converted to ammonia which can be used by organisms through a process called nitrogen fixation. The formed ammonia is oxidized by bacteria to first form nitrites that will be further oxidized to nitrates (nitrification). The absorption of nitrate by plants incorporates the nitrogen in proteins, nucleic acids and chlorophyll, which will be further converted to nitrogen-based animal compounds when assimilated by animals. The nitrogen cycle is closed by the denitrification process, where bacteria reduce nitrates to  $N_2$ , which is freed back into the atmosphere.



**Figure 1.1:** Simplification of the nitrogen cycle. Adapted from ref. <sup>1</sup>

The main cause of the destabilization of the nitrogen cycle is the usage of fertilizers, which contain large amounts of nitrates, causing environmental issues like the contamination of groundwater. Governmental regulations limit the maximum concentration of nitrate in drinking water to 10 mg/L <sup>17</sup>. However, the overpass of this limit in certain regions<sup>18</sup> leads to a need for nitrate removal from water. As the natural process of denitrification is unable to handle the excess of nitrite-derived substances, several methods to remove  $\text{NO}_3^-$  ions from contaminated water have been developed. Physicochemical methods like electrodialysis<sup>19</sup>, ion exchange resins<sup>20</sup> or reverse osmosis<sup>21</sup> only provide a separation method but do not convert nitrate. Biological methods<sup>22</sup> are slow and difficult to control and cannot be used for high nitrate concentrations to avoid poisoning the bacteria. These methods are hardly acceptable for large-scale applications due to the low reaction rate, continuous monitoring and/or large amounts of by-products. Electrochemical reduction of nitrate presents an alternative and promising solution, because it is selective, environmentally friendly and cost-effective<sup>23</sup>. Nitrate can be used as starting material to produce useful chemicals such as ammonia, hydroxylamine, hydrazine or azide. The intricacy of the electrochemical reduction of nitrogen-containing compounds is related to the existence of numerous stable species with

oxidations states from -3 to +5. The electrochemical reactions and their equilibrium potentials for the formation of the different reduction products are listed below<sup>24</sup>:



The obtained product varies depending on the cathode material, the electrolyte used and the potential applied<sup>25-29</sup>. Platinum has been the most studied catalyst for nitrate reduction. The reaction is pH dependent, being active in acidic media with the consequent formation of ammonium, but inactive at higher pH<sup>26</sup>. In addition, nitrate reduction on platinum in acidic media is surface structure dependent due to the structure-sensitive adsorption of hydrogen and anions<sup>30-31</sup>. Other metals such as rhodium show high activity for nitrate reduction over a wide pH range<sup>32-33</sup>, forming ammonium in acidic medium and nitrite in alkaline media<sup>34</sup>. Some coinage metals like Cu, Ag and Au have also been studied in acidic media<sup>35</sup>: among these metals, copper showed the highest activity for nitrate reduction, with ammonia as the main product<sup>29</sup>. The high activity observed for nitrate reduction on copper in alkaline media<sup>36-37</sup> makes it an interesting system due to the less probable formation of products like toxic nitrogen oxides compared to reduction in acidic media<sup>38</sup>. In this thesis, we investigated the mechanism of nitrate reduction on copper electrodes in acidic and alkaline media by cyclic voltammetry, Fourier Transform Infrared Spectroscopy, Ionic Chromatography and Rotating Disc Electrodes. Copper single crystals were used to unravel the structure sensitivity of the reaction (Chapter 2).

## 1.5 Electrocatalytic reduction of CO<sub>2</sub>

The accelerated increase of the population in the last century has resulted in a massive growth of energy consumption. 85 % of the world's energy demand is supplied by fossil fuels, the consumption of which creates an increase of greenhouse gases (GHG) in the atmosphere<sup>39</sup>. An increase of atmospheric levels of GHG creates environmental issues such as climate change. Although GHG such as methane and chlorofluorocarbons have much higher greenhouse effect per mass of gas, carbon dioxide is the largest contributor to global warming due to the substantial amounts present in the atmosphere<sup>40</sup>. Several strategies can be used to decrease the atmospheric CO<sub>2</sub> levels. First of all, one can reduce the world's energy consumption by means of more energy-efficient processes. Reduction in the carbon intensity of energy usage can be achieved by switching to renewable energies such as wind, solar or geothermal. Another option would be the capture and sequestration of CO<sub>2</sub><sup>41</sup>. However, this is a rather expensive option, and only provides a mid-term solution. A good strategy to make CO<sub>2</sub> capture more interesting would be to convert it to valuable chemicals and fuels by electroreduction<sup>42</sup>. The use of CO<sub>2</sub> as a C1 feedstock for the formation of more valuable chemicals offers the use of an easy, available and renewable carbon source, which is non-toxic and abundant. However, CO<sub>2</sub> is the most oxidized state of carbon, being thermodynamically and kinetically stable, such that it requires a large energy input to convert it into other molecules. The energy necessary for the electrochemical conversion can be obtained by renewable energies, making the combination of renewable energies with the electrochemical reduction of CO<sub>2</sub> a promising path towards a sustainable energy future with net neutral CO<sub>2</sub> emissions.

A significant amount of molecules can be formed from electroreduction of CO<sub>2</sub> especially on copper electrodes. In this thesis, we focus our attention on the formation of hydrocarbons such as methane, ethylene and ethanol and on the formation of bigger molecules such as cyclic

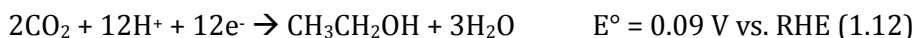
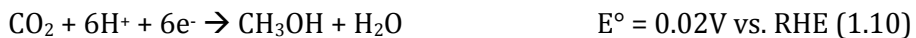
carbonates. Ethylene is a widely used industrial building block, and ethanol is a valuable fuel. Therefore, the reduction towards these desired products is potentially interesting, due to their higher energy density compared to single carbon products. The formation of cyclic carbonates offers wide applications in the chemical industry, as these are used as fuel additives, in plastics, as green solvents and as electrolytes for Li ion batteries.

### 1.5.1 Electroreduction of CO<sub>2</sub> to hydrocarbons

The electrochemical reduction of carbon dioxide has gained extraordinary interest in the past decades as a means of energy storage.

The simplest products obtained are those for which only 2 e<sup>-</sup> transfers are involved in the reaction path, such as carbon monoxide and formic acid. However, the formation of hydrocarbons would be the most significant target of CO<sub>2</sub> utilization due to their high energy density and the benefit of direct use without changing the present infrastructures based on fossil fuels.

The electrochemical reactions and their equilibrium potential for the formation of different products of carbon dioxide reduction are listed below:



The product distribution resulting from the electrochemical reduction of CO<sub>2</sub> depends on the metal used as electrode. A screening of several transition metals used for carbon dioxide was performed and a classification regarding the product formed was suggested<sup>43</sup>. The product selectivity is mainly determined by how CO<sub>2</sub> is reduced initially at the electrode surface. In the first group belong metals such as In, Sn, Hg and Pb that selectively form formic acid. These metals have high hydrogen overvoltage and low CO adsorption strength, therefore the intermediates are weakly adsorbed on the surface making those metals unable to catalyze the breaking of the C-O bond in CO<sub>2</sub> and thus facilitating the formation of formic acid. The second group of metals, where Ag and Au belong, produces mainly CO. CO is formed on these metals, especially on Au, at less negative potentials than formic acid. Hansen et al<sup>44</sup> developed a model to describe trends in catalytic activity for CO<sub>2</sub> reduction in terms of the adsorption energies of the reaction intermediates. Considering that CO is formed through the adsorbed intermediates \*COOH and \*CO, Au is able to stabilize \*COOH without over-stabilizing CO. This explains the formation of CO on Au at lower potentials than formic acid formation suggesting a different mechanism for the formation of CO. The third group consists of metals such as Ni, Fe, Pt and Ti, which evolve hydrogen at low potentials. On these metals CO<sub>2</sub> is reduced to CO, but it is strongly adsorbed on the surface, poisoning the metal and blocking possible further reactions. Therefore, the main product formed is hydrogen from the competitive hydrogen evolution reaction. Metals with a moderate CO adsorption energy are able to further reduce CO to hydrocarbons. Elements such Mo and Ru have been reported to convert CO<sub>2</sub> to methanol and methane but with low efficiencies<sup>45-46</sup>. However, copper is a unique metal able to form hydrocarbons, mainly methane and ethylene with high efficiencies<sup>47</sup>. Formation of oxygenated species such as ethanol and propanol has also been observed, although normally in smaller amounts<sup>48-49</sup>. Jaramillo et al. recently observed the formation of 16 different products: besides the main products such methane, ethylene, formate, CO, ethanol and propanol, other minor products such as allyl alcohol, methanol,

glycoaldehyde, acetaldehyde, ethylene glycol, propionaldehyde, acetone, acetate and hydroxyacetone were also observed with lower efficiency<sup>50</sup>. The extraordinary ability of copper to form hydrocarbons has motivated a substantial effort to understand its special activity for the carbon dioxide reduction reaction. Numerous experimental and theoretical studies have proposed mechanisms for the reduction of CO<sub>2</sub> on copper<sup>48, 50-56</sup>. However, a detailed mechanism for this reaction is still under debate<sup>49, 51-52, 57-58</sup>. Ethylene and methane formation follow two different pathways<sup>59</sup> having carbon monoxide as the key intermediate in the formation of both products<sup>60-62</sup>. The formation of methane has been found to be pH dependent<sup>61, 63</sup>, which implies that the rate-determining step must involve the transfer of a proton and an electron. Hori suggested a path for the formation of methane via adsorbed COH<sup>61</sup>. In contrast, the formation of ethylene is pH independent,<sup>61, 63</sup> which implies that the rate-determining step does not involve a proton transfer. However, the formation of ethylene does depend on the potential, so that an electron transfer must be involved. A C-C coupling of two adsorbed CO molecules through a reductive dimerization step has been proposed as a rate-determining step<sup>51, 57</sup>. In chapter 4 of this thesis the formation of this CO dimer will be discussed in detail.

Several factors such as the electrode morphology<sup>47, 64</sup>, the pH of the electrolyte<sup>63</sup>, the identity of the cations and anions<sup>56, 65</sup>, the size and shape of nanoparticles<sup>66</sup>, the oxidation state of the copper electrode<sup>67</sup>, among others, have been extensively studied to gain insight into the extraordinary reactivity of copper to form hydrocarbons from carbon dioxide.

In this thesis, we focus our attention on the study of several steps during the reduction of CO<sub>2</sub> such as the reduction of CO (chapters 4 and 5) and the reduction of acetaldehyde (chapter 3) in order to gain insight into the mechanism of the reaction. In addition we investigated how different factors such as the structure of the electrode, the potential applied or/and the effect of the cations influence the mechanism of these reactions. The study was performed with a combination of

techniques such as cyclic voltammetry, High Performance Liquid Chromatography, Online Electrochemical Mass Spectrometry, Fourier Transform Infrared Spectroscopy and Density Functional Theory calculations.

### **1.5.2 Electroreduction of CO<sub>2</sub> to cyclic carbonates**

Cyclic carbonates are profitable synthetic targets starting from CO<sub>2</sub> due to the added value of these organic molecules compared to CO<sub>2</sub>. In addition, the fixation of CO<sub>2</sub> into organic molecules offers an environmentally friendly alternative to storage solutions<sup>68</sup>. The formation of cyclic carbonates has been an area of interest due to the versatility of these compounds. Cyclic carbonates can be used as electrolytes for Li ion batteries, fuel additives, as aprotic polar solvents, as green reagents and as useful intermediates for manufacturing polycarbonates<sup>69-70</sup>. Polycarbonates are the most widely used engineering plastics, currently synthesized through the phosgene process. The use of a highly toxic substance like phosgene, which is regulated by the international treaty concerning chemical weapons<sup>71</sup>, makes the synthesis of polycarbonates environmentally unacceptable. Substituting phosgene with CO<sub>2</sub> will radically diminish environmental issues due to not only the elimination of toxic by-products but also due to the capture and conversion of CO<sub>2</sub>.

In view of the commercial importance of cyclic carbonates and their broad applications in industry, the catalytic synthesis of these compounds has been extensively studied. Several homogeneous catalysts based on metal complexes<sup>72-74</sup> have been proposed for the conversion of CO<sub>2</sub> and epoxides to cyclic carbonates. However, most of the currently used catalysts for this process demand high operational temperatures and/or high carbon dioxide pressures<sup>75-77</sup>. The use of electrochemistry allows for the synthesis of cyclic carbonates under mild conditions with high efficiencies<sup>78-79</sup>. Copper, among other metals tested for this process such as Ni, Ag or graphite, has been found to be

one of the most efficient metals for the conversion of carbon dioxide and epoxides to cyclic carbonates<sup>79-81</sup>. Copper and copper nanoparticles have been employed as cathode for the synthesis of cyclic carbonates, achieving high conversion and selectivity<sup>78,80</sup>.

Despite all the studies concerning this process, the mechanism of the reaction is still under debate. While numerous studies argue that the key step for the synthesis of cyclic carbonates is the activation of the epoxide via the ring opening<sup>72, 74, 82-83</sup>, other studies consider the activation of carbon dioxide through the formation of the radical anion  $\text{CO}_2^-$  to be the key step for the synthesis of organic carbonates<sup>81,84</sup>.

In this thesis, we employed Fourier Transform Infrared Spectroscopy (FTIR) and High Performance Liquid Chromatography (HPLC) to gain insight into the mechanism of cyclic carbonates synthesis and establish that adequately activated  $\text{CO}_2$  is able to carboxylate organic molecules, such as epoxides, to form cyclic carbonates.

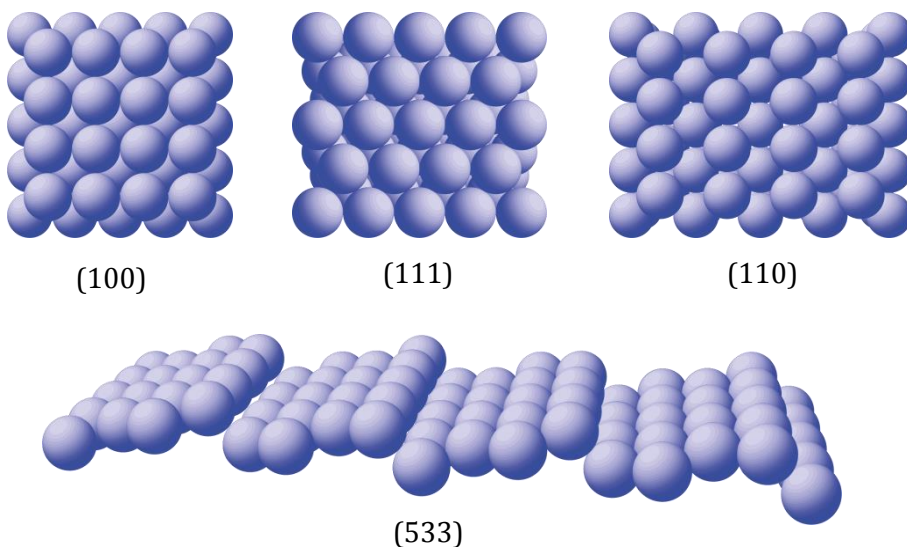
## **1.6 Copper, an extraordinary catalyst**

Copper has been used since 8000 BC due to the luxury of direct use in metallic form without its extraction from an ore. Copper is abundant on Earth, with  $10^{14}$  tons existing in the first kilometer of the Earth's crust. The abundance of copper and its ease of mining make it a rather inexpensive metal. The price of copper has been unstable during history<sup>85</sup>, although in the last 10 years it has been more stable with values around US\$3/kg. The price of copper is more than 10000 times lower than other metals like Pt or Au. The abundant and cheap nature of copper, has generated interest into its use as a catalyst in electrochemical processes. Metallic copper, copper-based and oxide-derived copper catalysts are able to efficiently catalyze numerous reactions<sup>29,47,57,67-68,86</sup>. In this thesis, we will focus our attention on the reduction of nitrates, the reduction of carbon dioxide and the

conversion of carbon dioxide and propylene oxide to propylene carbonate on metallic copper electrodes.

The morphology of the catalyst is crucial to understand the mechanism of the reaction carried out on the copper surface. For that reason, copper single crystals were employed.

Copper is a face-centered cubic (fcc) metal with copper atoms located at each of the corners of the unit cell and at the center of all the cubic faces. Bulk copper has a coordination number of 12 since 12 of their atoms are shared with other unit cells. The fcc unit cell consists of a net total of four atoms, eight eighths from corner atoms and six halves from the face atoms. In order to identify the different planes and directions in a crystal structure, Miller indices are used which consist of three values of  $h$ ,  $k$  and  $l$  as directional parameters. The most studied surfaces are those for which the plane is perpendicular to the principal axis, called basal planes. For an fcc structure the basal planes are (100), (111) and (110). In addition, other surfaces with larger Miller indices, namely stepped surfaces, can also be studied. Ideal stepped surfaces consist of terraces



**Figure 1.2:** Representation of different surface structures of an fcc crystal, taken from surface explorer.(<http://surfexp.fhi-berlin.mpg.de>)

with a low index atomic arrangement, separated by monoatomic steps. A representation of such surfaces is displayed in Figure 1.2. The use of single crystals in electrochemistry helps in understanding how different adsorption sites influence the stability of intermediates in a certain reaction, catalyzing more efficiently the conversion of different species.

## **1.7 Scope and outline of this thesis**

The general focus of the research offered in this thesis is the electro-conversion of environmentally harmful chemicals, such as nitrates and carbon dioxide, into more valuable and less polluting compounds. In particular, the study is focused in the understanding of the mechanistic aspects of these reactions carried out on copper electrodes.

In chapter 2, we study the electrochemical reduction of nitrates on copper single-crystal electrodes in acidic and basic media to evaluate the reaction mechanism and the products obtained in the different media and on the different surfaces employed. Using electrochemical techniques coupled to analytical techniques we observe differences in product distribution depending on the pH of the electrolyte. Whereas in acidic media the reduction of nitrate leads to NO and ammonia, in basic media the product observed is hydroxylamine. Furthermore, the reaction is structure sensitive in basic media: Cu(100) is most active for the formation of hydroxylamine. Conversely, in acidic media the reaction is independent of the catalyst's structure.

In chapter 3 we study the electroreduction of acetaldehyde to ethanol, a reaction which is supposed to take place at a late stage in the reduction of carbon dioxide. Combining experimental techniques with density functional theory we outline the structure sensitivity of the reaction. Experiments show that more open facets have lower overpotentials for the formation of ethanol. DFT calculations predict that the formation of ethanol proceeds via a weakly bounded  $\text{CH}_3\text{CH}_2\text{O}^*$  intermediate which binds more favourably on open surfaces, explaining the earlier

formation of ethanol on those facets. In addition, DFT calculations show higher thermodynamic limitations for ethanol compared to ethylene. Making use of the structure selectivity observed for ethanol formation, the selectivity towards ethanol formation can be enhanced.

In chapter 4 we study the early stages of CO reduction by Fourier Transform Infrared Spectroscopy and Density Functional Theory. We show experimentally that Cu(100) electrodes in LiOH solutions host a C-containing adsorbate at low overpotentials, which we propose to be a hydrogenated CO dimer (OCCOH). The formation of the hydrogenated dimer is a structure-sensitive process, which does not occur on Cu(111) surfaces, confirming the theoretical hypothesis that the dimerization is favoured on square-symmetry sites.

In chapter 5 we show how the combined effect of alkaline cations, catalyst structure and applied potential can steer the selectivity of CO reduction towards ethylene or methane. First, we find that the nature of the cation affects the product selectivity, depending on the potential applied. Whereas larger cations enhance the selectivity to ethylene at potentials more positive than -0.45 V vs RHE, the selectivity towards methane is enhanced by larger cations at more negative potentials. The fact that ethylene formation declines at potentials for which methane formation increases, suggests that the pathway towards ethylene is blocked by the enhancement of the pathway that leads to methane. Secondly, we observe that cation effects are structure dependent, as the onset potential for ethylene formation depends on the electrode structure and cation size, whereas the onset potential for methane formation does not. The formation of the intermediate suggested in chapter 4 (OCCOH) was found to be dependent on the nature of the cation, so that the hydrogenated dimer can be detected with FTIR in presence of Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup>, but not in presence of Rb<sup>+</sup> or Cs<sup>+</sup>. DFT calculations explain that the potential necessary to form \*OCCOH from \*CO in presence of Cs<sup>+</sup> is more negative compared to Li<sup>+</sup> or Na<sup>+</sup>. Lastly, we point out the role of the cations as catalytic promoters by stabilizing intermediates through favourable electrostatic interactions.

In chapter 6 we investigate the conversion of CO<sub>2</sub> to organic molecules, specifically the reaction between CO<sub>2</sub> and propylene oxide to form propylene carbonate. Employing cyclic voltammetry, Fourier Transform Infrared Spectroscopy and High Performance Liquid Chromatography we study the mechanism of the reaction. We rule out different reduced forms of CO<sub>2</sub>, such as CO and (bi)carbonate as possible carboxylation agents. Moreover, we rule out the electrochemical activation of propylene oxide via ring opening as the initial step for this reaction. We propose an electrochemical reaction initiated by the activation of CO<sub>2</sub> to CO<sub>2</sub><sup>-•</sup> which then attacks propylene oxide to form propylene carbonate.

