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## Promotion of the Electrocatalytic Reduction of Nitrate

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# Introduction

## 1.1 Nitrogen Cycle

At the beginning of this thesis, we give a brief review on the nitrogen cycle that is of importance for the remainder of the thesis.

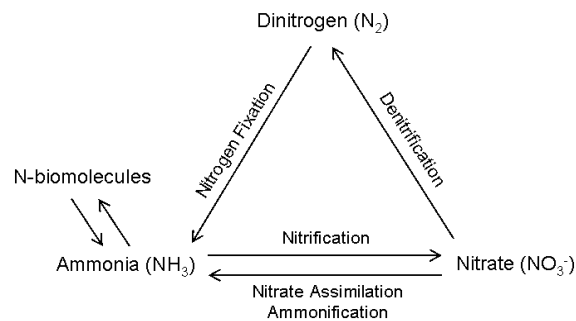


Figure 1. Biogeochemical nitrogen cycle. Adapted from ref.<sup>1</sup>

Nitrogen is a key element for most living things on this planet: it is a major component of chlorophyll that is important pigment for photosynthesis, of amino acids that are the key units of proteins, as well as of nucleic acids that encode, transmit and express genetic information.<sup>2</sup> Although nitrogen gas is abundant in the atmosphere, it is very inert and not directly usable to plants. Whereas ammonia and nitrate are basic nutrients of nitrogen that can be easily absorbed by plant roots, their natural availability is limited. The abundance of their salts in soil is largely dependent on the geographic property of given region. On the other hand, lightning and ultraviolet radiation can cause the chemical fixation of atmospheric dinitrogen to inorganic nitrogen molecules such as ammonia, nitrogen oxides or nitrate, particularly in the upper atmosphere, where the formed nitrogen nutrients can precipitate down to ground by rain, contributing to the total N-input from atmospheric dinitrogen. However, it is unlikely to support the diversity in

biosphere by chemical fixation of dinitrogen; only microorganisms can perform the important role of inputting atmospheric dinitrogen to the ecosystem, by which some 40% of the total N-input in soil and water nowadays is achieved,<sup>3</sup> maintaining the nitrogen cycle in the biosphere that is accomplished by specific microorganisms in different processes. In this biochemical cycle, ammonification occurs as a process of autolysis, decay and putrefaction of biological materials to form ammonia. Nitrification is to oxidize ammonia to nitrite and nitrate to harvest energy for the synthesis of organic matter for microorganisms themselves. Denitrification is to convert nitrate to dinitrogen as the end product, by which organic matter donates electrons to release energy. Nitrogen fixation is carried out to convert atmospheric dinitrogen to a usable form such as ammonia so that the loss of nitrogen to the atmosphere in the process of denitrification is compensated.<sup>3</sup> Microorganisms that can fix atmospheric dinitrogen may be free-living or in symbiotic association with plants.<sup>4</sup> However, it is more important in agriculture for the association between legumes of crops and microorganism that can develop nodules in the root system of leguminous plant,<sup>5</sup> which was firstly discovered by the Dutch microbiologist Martinus Willem Beijerinck in 1888, and who also established the conception of biological nitrogen fixation later in 1901.<sup>6,7</sup> However, this natural process is quite limited to specific microorganisms and plants, and recycling the organic waste to crops is too slow and inefficient to input enough nitrogen. Therefore, nitrogen was deemed as the limiting nutrient element during pre-industrial agriculture.<sup>8</sup>

However, the situation changed when in 1909, the German chemist Fritz Haber filed a patent of his groundbreaking discovery on the "synthesis of ammonia from its elements", and in 1913, the German chemist and engineer Carl Bosch successfully scaled it up to an industrial-level commercialization, now known as the Haber-Bosch process.<sup>8</sup> This marked a new era in human history for making feasible the large-scale production of ammonia with raw resources, atmospheric nitrogen and natural gas, that are abundant and easily available. More importantly, the synthesized ammonia can be used as raw material to produce other nitrogen compounds, such as nitrate. Consequently, the natural deposit of nitrate, saltpeter, is no longer a source for industrial needs, since there are many uses for nitrate in modern society. For instance, nitrate can be used as additive to food,<sup>9</sup> in explosives, and used to relax and widen the blood vessels in the body to prevent and relieve chest pain (angina) that is induced by the coronary artery disease,<sup>10</sup> and to synthesize hydroxylamine that is a raw material for Nylon production.<sup>11-13</sup> In 2

application of nuclear energy, a large amount of nitric acid is used in the reprocessing of plutonium resulting in radioactive waste containing nitrate.<sup>14</sup> However, the most important use of nitrate is as fertilizer. Nitrate salts,  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  for instance, are commonly preferred as nitrogenous fertilizers in agriculture. Since 1950, the rapid popularization of nitrogenous fertilizer application has increased the worldwide consumption of nitrogen fertilizer and contributed to the supply of enough foods for the growing world population.<sup>8, 15</sup>

## 1.2 Environmental Issues

Unfortunately, the balance of natural nitrogen cycle is disturbed because of the inefficient management of uses of nitrate and their wastewater treatment in some areas, as well as the extensive tail-gas of combustion of fossil fuels. The surplus of nitrate from agricultural running-off and wastewater enters into the surface water ecosystem, where the slow natural process of self-purification is unable to deal with all nitrate. Consequently, algal bloom results in a depletion of dissolved oxygen and also reductive formation of toxic compounds below the water surface, such as hydrogen sulfide, so that aquatic animals can not survive.<sup>16</sup> Meanwhile, the blooming algae can release a potent hepatotoxin called microcystin,<sup>17, 18</sup> which can impair the ability of aquatic animals to survive, grow and reproduce, and also cause severe damage on the liver of human beings.<sup>19, 20</sup> Moreover, the ingested nitrate or nitrite in drinking water directly threatens public health by inducing methemoglobinemia particularly in young infants, and also a potent cancer of digestive tract and other diseases.<sup>21</sup> Therefore, the amount of nitrate in drinking water is regulated to be below 50 mg nitrate ion/liter (11 mg nitrate nitrogen/liter) in Europe Union and 44 mg nitrate ion/liter (10 mg nitrate nitrogen/liter) in the United States.<sup>9</sup>

The excessive nitrate derived from nitrogen fixation causes severe threats on environment and human health now. Therefore, it is very important to offset the nitrogen inflow to the ecosystem and to selectively reduce nitrate back to  $\text{N}_2$  from waste- and groundwater.<sup>22</sup> Currently, besides the physical separation of nitrate from water, the main methods that are applied to treat nitrate-containing wastewater are to convert nitrate in a biological or chemical process. However, the general basis of these processes is kind of redox reactions that need to be catalyzed to obtain a specific selectivity or higher activity. In the next section, the

biochemical, chemical and electrocatalytic reduction of nitrate are summarized with consideration of their redox catalysis.

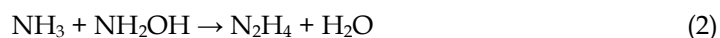
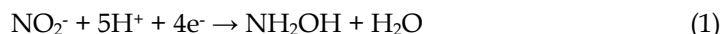
### 1.3 Nitrate Reduction

#### 1.3.1 Biochemical reduction

In microbial metabolism, nitrate reduction can be categorized as denitrification (to form dinitrogen) and ammonification (to form ammonia), based on the final product in the pathway, or as dissimilatory and assimilatory processes, based on the purpose of nitrogen transformation for energy conservation, detoxification or biosynthesis.<sup>1</sup> However, the microbial reduction of nitrate is carried out by enzymes that specialize in catalyzing specific steps in the overall reaction. Taking bacteria (prokaryotes) for example, three distinct nitrate reductases that catalyze the nitrate reduction to nitrite have been identified. Two of them are related to respiratory electron transport by coupling to quinol oxidation: respiratory nitrate reductase (Nar) anchors to the cytoplasmic face of membrane; periplasmic nitrate reductase (Nap) locates in periplasmic compartment. A third one is assimilatory nitrate reductase (Nas) that is a cytoplasmic enzyme and is involved in nitrogen assimilation.<sup>23, 24</sup> In eukaryotes, the assimilatory nitrate reductase (Euk-NR) localizes in the cytoplasm and is also related to the formation of ammonia.<sup>25</sup> In denitrifying prokaryotes, the catalytic subunit of those nitrate reductases generally contain a mononuclear Mo center, where one molecule of nitrate is coordinated to form nitrite with electron transfer mediated by metal cofactors such as Fe-S clusters and hemes.<sup>26</sup> Nitrite reductase catalyzes nitrite reduction to NO and two distinguishable reductases have been identified. In cytochrome *cd<sub>1</sub>*, heme *c* mediates electron transfer to the catalytic center of heme *d<sub>1</sub>* where nitrite is bound. In copper enzyme, two types of Cu centers respectively bind nitrite and complete intramolecular electron transfer.<sup>27</sup> Nitric oxide reductase catalyzes the reductive dimerization of NO to N<sub>2</sub>O, where the heme *c* center accepts electrons from external electron donor and the heme *b* center mediates intramolecular electron transfer to binuclear catalytic centers of heme *b* and non-heme Fe that binds NO.<sup>28</sup> Nitrous oxide reductase finally catalyzes the reduction of N<sub>2</sub>O to N<sub>2</sub> and has two types of Cu centers: a binuclear Cu center as electron transferring center and a tetranuclear copper sulfur center (Cu<sub>4</sub>S<sub>2</sub>) as catalytic center.<sup>29</sup>

Another important and special process of denitrification is anaerobic ammonia oxidation (ANAMOX), where bacteria can use ammonia as an electron donor and

nitrite as an electron acceptor.<sup>30</sup> The reaction pathway has been described as follows:



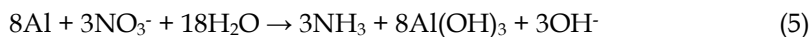
Thus, the overall reaction is:



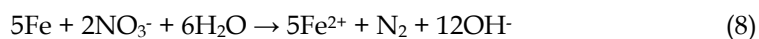
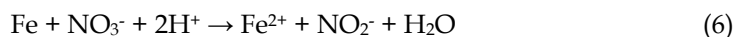
Interestingly, a similar mechanism has been evidenced in research of nitrite reduction by platinum.<sup>31</sup>

### 1.3.2 Chemical reduction

As an active oxidant, nitrate can be reduced in a chemical reaction with a reductant, normally metals or molecules.<sup>32</sup> For active metals, the chemical process is strongly related to the solution pH. Taking aluminum as an example, the observed reaction only takes place when solution pH is above 8 and prevails in the pH range of 9 to 10, where the principle reaction is to form ammonia, as given in reaction (5), with a little formation of nitrite and dinitrogen.<sup>33</sup>



On the other hand, iron only performs effectively in acid range and again ammonia is found as the main product.<sup>34</sup> Iron nanoparticles have also been investigated for nitrate abatement in a batch experiment.<sup>35, 36</sup> The reaction pathways are suggested as follows:

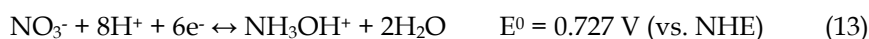
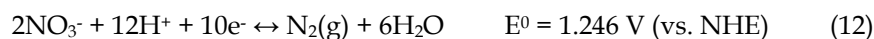
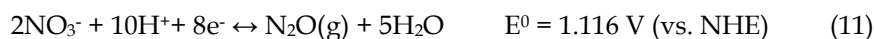


However, the chemical reactions between nitrate and iron will result in a positive pH shift. A buffer solution is necessary to maintain the activity of chemical reactions. Moreover, there is a side reaction between metal and acid solution that results in H<sub>2</sub> formation at the same time, which results in the increase of consumption of metal and also unnecessary metal cations in water.

Furthermore, borohydride, formic acid and hydrogen, are molecular reducing reagents that are able to react with nitrate.<sup>32</sup> In contrast to the above discussed stoichiometric reduction, this kind of chemical reaction normally requires a homogeneous or heterogeneous catalyst in solution, to achieve an enhanced activity and selectivity to some products. A good catalyst for this kind of catalytic reduction of nitrate is a Pd-Cu bimetallic catalyst, on which the Cu sites take care of the hydrogenation of nitrate to nitrite and N<sub>2</sub>O, and the specific formation of N<sub>2</sub> is suggested to be related to Pd sites.<sup>37</sup> In addition, bimetallic catalysts such as Pd-Sn and Pd-In can enhance the selectivity to form N<sub>2</sub>, which is observed to depend on solution pH.<sup>38</sup>

### 1.2.3 Electrocatalytic reduction

Electrochemistry is the branch of chemistry that studies chemical species and reactions that take place at the interface between electrode and electrolyte, where electron transfers occurs. The rate and the direction of electron transfer can be controlled by the potential of the electrode. By changing the nature and the catalytic properties of the electrode surface, activity and selectivity can be steered simultaneously. On the working electrode, the nitrate reduction happens step by step to form different nitrogen species, dependent on the electrode potential, and the equilibrium potentials for each product are listed below<sup>39</sup>:



Platinum, both polycrystalline and single crystalline, is the most investigated electrode material for nitrate reduction, although other materials, both coinage and noble metals, have been studied as well and have been found to show a different activity.<sup>40</sup> However, nitrate reduction on Pt is not very active. The first step of nitrate reduction to nitrite is suggested as the rate determining step in the overall reaction and the direct reduction of nitrate selectively gives rise to ammonia formation as the only end-product.<sup>40, 41</sup> Therefore, to obtain an enhanced nitrate reduction activity and selectivity to certain nitrogen product (N<sub>2</sub> and

hydroxylamine being the most interesting), the research on electrocatalytic reduction of nitrate on a bimetallic electrode, where the electrode surface is modified by a foreign metal, has been given special attention.<sup>39</sup> Moreover, modern analysis techniques can be combined with electrochemistry, which greatly enhances the capacity of electrocatalysis in the research of nitrate reduction. Therefore, it is a promising and challenging to search for a well performing catalyst and to unravel its corresponding catalytic mechanism, which is the main aim of this thesis.

## 1.4 Research in This Thesis

In this thesis, the electrocatalytic reduction of nitrate is investigated on noble metals, Pt and Rh, especially in the presence of foreign modifiers, to elucidate the influence of several important factors, such as electrode surface, solution pH and anions. The selective formation of volatile and nonvolatile products will be studied and the suggested reduction mechanism will be discussed.

In Chapter 2, the enhancement of nitrate reduction by Sn modifier on polycrystalline Pt in acid medium is investigated. By comparing different coverages of Sn species, a distinct selectivity to volatile products is revealed. Furthermore, homogeneous side reactions between intermediates near the electrode, both during voltammetry and amperometry, are an important factor in generating volatile products.

As Sn shows a strong promoting effect on nitrate reduction on a polycrystalline Pt electrode, Chapter 3 studies the existence of a general trend of catalyzing nitrate reduction by p-block metals on polycrystalline Pt electrode, where Sn is categorized within the periodic table of elements. Thus, a comparative study on nitrate reduction with p-block metals as foreign modifiers on polycrystalline Pt electrode is carried out in both perchloric and sulfuric acid medium, focused on the formation of volatile products. The study shows that Sn shows a unique capacity to promote nitrate reduction on Pt. With the advance of combining ion chromatography with voltammetry, the nonvolatile products from nitrate reduction on Pt and Sn-modified Pt electrodes are detected concurrently with the voltammetry in Chapter 4. Interestingly, Sn also steers the selectivity to form hydroxylamine as the main non-volatile product of nitrate reduction in acid medium.

Since the solution pH is an important factor in the nitrate reduction, Chapter 5 studies the details about the influence of solution pH on nitrate reduction on Rh and Pt electrodes in a broad pH range. Rh shows a higher catalytic activity for nitrate reduction in the entire pH range compared with Pt, especially in alkaline media. The pH dependence will be explained by two different activation pathways for nitrate reduction.

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