Electrocatalysis of the nitrite reduction : a mechanistic study

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Introduction

1.1 General introduction to the thesis

This thesis deals with the mechanistic investigation of the electrocatalytic nitrite reduction. Nitrite is a well-known threat to human health[1-4], being a potential carcinogenic agent and the main cause of the so-called "blue baby syndrome"[1]. Therefore, its levels must be carefully monitored in drink- and groundwater[5], where nitrite often occurs as a widespread pollutant. Usually, nitrite is removed with biological treatments ("active sludge")[6-10], which however could harbor pathogenic bacteria; therefore, among the alternative catalytic treatments[11], electrocatalysis[12,13] could come to the fore provided that sufficient activity and selectivity to harmless (N_2) or industrially valuable molecules (NH_2OH)[14] is achieved.

To appreciate the relevance of nitrite in the (electrochemical) nitrogen cycle, a brief foray into the Earth's biogeochemical nitrogen cycle is worthwhile.

1.1.1 The biogeochemical nitrogen cycle: a historical perspective

The biogeochemical nitrogen cycle owes its complexity to the many interconnected processes that involve the various interacting environmental compartments. As Figure 1 shows, the atmosphere, the biosphere and the geosphere all take part in the nitrogen cycle, along with the ever increasing anthropogenic contribution[15].

Section 1.3 of this chapter is based on the review: Rosca, V.; Duca, M.; de Groot, M. T.; Koper, M. T. M. *Chem. Rev.* **2009**, *109*, 2209-2244.

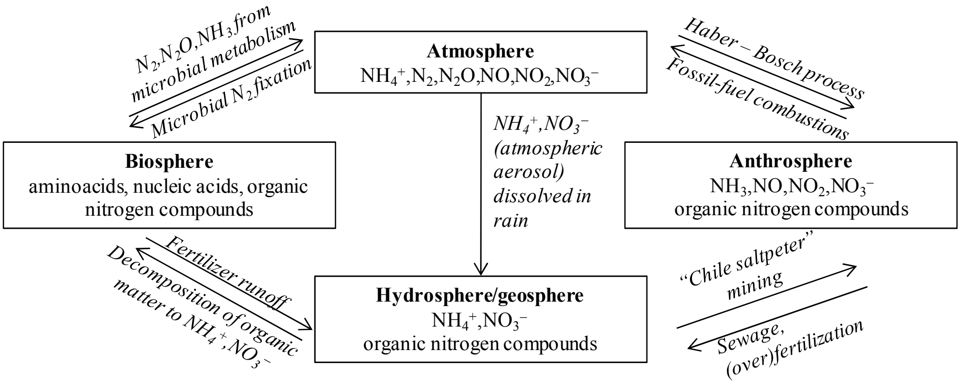

Figure 1 The nitrogen cycle. Adapted from reference 1.

Before analyzing the current cycle in details, we should briefly follow the history of the nitrogen biogeochemical cycle[16,17]. In fact, it has undergone dramatic changes following Earth's evolution throughout the geologic ages. Nitrogen was present on the early Earth mainly as atmospheric N_2, if one neglects the minor contribution of NH_3 and nitrogen-containing organic compounds cast on the Earth from cosmic bodies such as comets (which is currently linked to the origin of life). N_2, degassed from the mantle via volcanic eruptions, is now thought to be the dominant molecule of the archaic atmosphere[17] that, in disagreement with previous models, was largely inert rather than reducing. For example, the famous Urey-Miller experiment[18] was carried out assuming that the early atmosphere was composed of CH_4, NH_3, H_2 and H_2O. Despite being largely inert, N_2 could be cleaved and form NO in lightning-induced reactions involving CO_2 [16]; further photochemical or aqueous-phase reactions produced NO_3^- in the early oceans. Solution-phase reactions involving Fe^{+2} as reducing agent are speculated to be a source of NH_4^+.

$$\text{(atmosphere)}\ N_2 + CO_2 \xrightarrow{\text{lightning}} NO \rightarrow \text{(oceans)} \rightarrow NO_3^- \xrightarrow{Fe^{+2}} NH_4^+ \qquad (1)$$

The appearance of primordial life was the cause of the first revolution of the nitrogen cycle. The scarce presence of NH_4^+, a fundamental source of nitrogen for the synthesis of aminoacids, which was a major limiting factor for bacterial growth, was bypassed by the evolution of two metabolic pathways that allowed microorganisms to produce NH_4^+ via these two reactions: the first, called *nitrate assimilation* (or *assimilatory denitrification*):

$$NO_3^- + 8e^- + 10H^+ \rightarrow NH_4^+ + 3H_2O \qquad (2)$$

and the second, the all-important *nitrogen fixation* (currently carried out by bacteria associated with leguminous crops):

$$N_2 + 6e^- + 8H^+ \rightarrow 2NH_4^+ \qquad (3)$$

The latter reaction emerged rather early, according to recent findings[19], and probably made use of iron- or vanadium-based enzymes called *nitrogenases*[20], given the large availability of these two metals in the early ocean[17]. Alongside, *dissimilatory denitrification* also emerged at a certain moment (the age of this process is disputed[17]), balancing atmospheric nitrogen fixation:

$$2NO_3^- + 10e^- + 12H^+ \rightarrow N_2 + 6H_2O \qquad (4)$$

A key enzyme of this pathway handles the toxic intermediate NO_2^- and enables its stepwise conversion to N_2; this nitrite reductase is based on a cytochrome[21], which is extremely sensitive to O_2. As a consequence, dissimilatory denitrification must have appeared before the so-called "great oxygenation event", subsequent to the onset of photosynthesis.

The accumulation of oxygen gave rise to the modern (pre-industrial) nitrogen cycle. Abiotic nitrogen fixation now occurs with the following reaction:

$$N_2 + O_2 \xrightarrow{\text{lightning}} 2NO \rightarrow\rightarrow NO_3^- \qquad (5)$$

which is 50 to 5000 times more efficient than (1). In addition, the availability of oxygen allowed some microorganisms to exploit NH_4^+ (from the decay of organic matter) as an electron source. This oxidative pathway, called *nitrification*, maintains a balanced nitrate content in the soil, which is of paramount importance for terrestrial plants.

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+ \qquad (6)$$

Figure 2 summarizes the pre-industrial (aerobic) nitrogen cycle.

1.1.2 Current imbalances – environmental issues.

The impact of human activities on the nitrogen cycle has dramatically increased since the beginning of the Industrial Revolution and there is growing consensus[17,22,23] that this cycle has suffered the largest imbalance[*] in the wider framework of the current geologic age, defined Anthropocene[24] by the Nobel Laureate P.J. Crutzen in 2002.

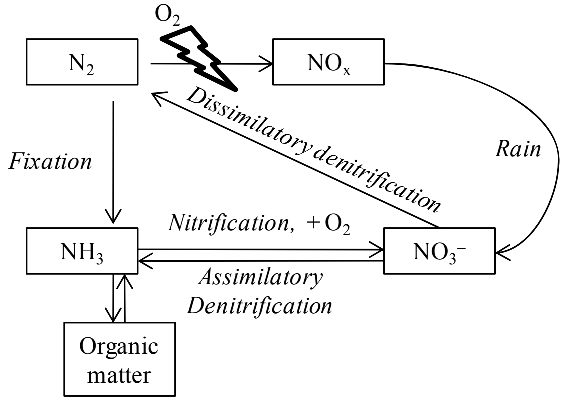

Figure 2 Schematic representation of the main reactions of the nitrogen cycle prior to the Industrial Revolution. Adapted from ref. 2.

The key concept in order to understand the human intervention, is the amount of "reactive nitrogen" (Nr) produced in a certain amount of time within a biogeochemical system. Nr, defined in the environmental sciences as "all biologically active, photochemically reactive and radiatively active N compounds in the atmosphere and biosphere of the Earth"[23] (thus excluding inert N_2), is the

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[*] The concept of "tipping point" is central to current research in the field of Environmental Sciences. Interdisciplinary studies modeling the Earth's cycles have shown that there is a critical threshold of human-driven imbalancing effect that, if surpassed, can bring about dramatic consequences, largely unpredictable with current models. This threshold has been defined as "tipping point". Reliable quantitative calculations of nitrogen fluxes[17,23] have shown that the current rate of Nr formation equals the 340% of the safety threshold, while, for example, the current atmospheric CO_2 concentration represents "only" the 110% of the safety threshold, and the well-known runoff of phosphorous-laden wastewater into water streams and oceans is below the tipping point at 83%. A suggested introductory reading for the layman is *Boundaries for a Healthy Planet*, *Scientific American*, **2010**, *302*, 38-41

fundamental tool to compute the human footprint on the nitrogen cycle because, as we have seen in section 1.1, natural conversion of N_2 into Nr has always been sluggish and rate-limiting. This steady state was dramatically altered by the development of the Haber-Bosch process, a high-pressure catalytic reaction[25] (using cheap, abundant iron as catalyst) which converted N_2 into NH_3, the active component in synthetic fertilizers:

$$N_2 + 3H_2 \xrightarrow{T,P} 2NH_3 \qquad (7)$$

Manmade fertilizers have since the invention of the Haber-Bosch process played a cornerstone role in feeding a growing population and sustaining its growth by supplying an ever increasing range of foodstuff for wholesome diets and the current level of world population would be unsustainable without artificial nitrogen fixation. Therefore, it seems appropriate to recall Sir Winston Churchill's famous statement: "Never have so many owed so much to so few". However, excessive fertilizer use and its runoff from field into groundwater have elicited an increasing concern about the polluting effects of Nr accumulation. Affected environments, usually humid or coastal areas, will develop algal blooms, so-called dead-zones[26] and loss of biodiversity; groundwater will be polluted by nitrates derived from microbial nitrification via reaction 6. On a planetary scale, volatile products of enzymatic reaction of soil microbes (the greenhouse gas N_2O), will contribute to the ongoing climate changes: its warming potential equals to 300 times that of CO_2, with additional ozone-disrupting properties[15,17,27]. Agriculture itself represents an additional contribution to Nr synthesis (amounting to 1/3 of the Nr contribution of the Haber-Bosch process[17]), mainly due to leguminous crops. Additional nitrogen fixation also occurs during fossil fuel combustion[28] (via reaction 5; quantified to 1/5 of Nr fixation via the Haber-Bosch process[17]) and is currently the main contributor to acid rain after successful policies aimed at reducing the sulfur content of coal and other fuels. Figure 3 summarizes the anthropogenic contributions to the current nitrogen cycle.

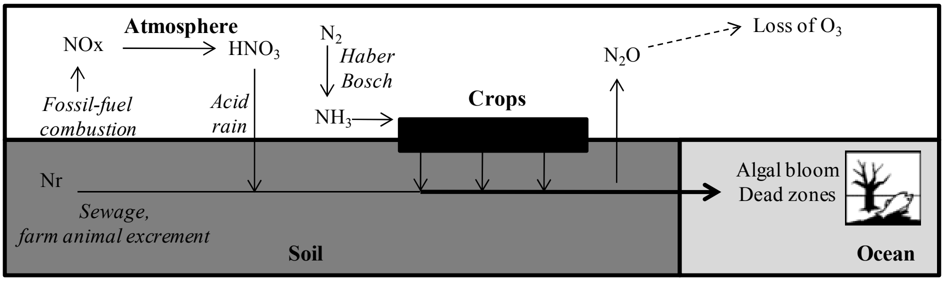


Figure 3 Anthropogenic contributions to the current nitrogen cycle. Adapted from ref. 8.

Quantitative data have been discussed in several papers[17,22,23]. The creation of Nr is steadily accelerating as a function of increasing cereal and meat production. For example, the amount of Nr created yearly was ca. 15 Tg N in 1860 compared to 187 Tg N in 2005; the Haber-Bosch process has contributed to fixation of 121 Tg N per year (2005)[23]. The Netherlands represent a typical case of fertilizer-intensive agriculture developed to meet the needs of the zootechnical industry for meat and milk production. The comparison between use of nitrogen-containing fertilizer and its ratio to the population of the Netherlands is extremely informative. In 1910, 6 million inhabitants used 13 k tonne of N fertilizer yearly, while 16 million people consume 400 k tonne N fertilizer per year nowadays, producing enough produce for a population of double size[23]. This means that the nitrogen fixed in food is partly exported, while the burden of the nitrogen lost in food production remains in the Netherlands and affects the local environment. This is only an example of the *geographical imbalances* of nitrogen production, distribution and accumulation, and current research devotes much attention to the spatial mobility of Nr species around the globe[17,23]. The outlook for the future of the nitrogen cycle in the Anthropocene will remain dire if no action is taken. Current global trends[17,22,23] are likely to worsen the imbalances described above: fertilizer-intensive practices such as growing fodder for livestock or the diffusion of many crops as raw materials for bio-fuels, along with mere population increase. The worldwide diffusion of intensive fertilizer-inefficient agricultural practices is extending the range of areas[22,23] blighted with nitrogen accumulation and nitrogen-enriched ecosystems in these areas will pose additional serious threats to the human health.

There is widespread consensus that no single technological breakthrough or worldwide policy can solve the imbalances of a cycle that comprises bacterial process having a slow feedback (if the rate of anthropogenic nitrogen fixation were stabilized now, a new steady state would emerge not earlier than 2050[17]). Many researchers and policy-makers agree on this roadmap for action[17,22,23]:

- Reimplementation of crop rotation
- Reduced fertilizer application via micro-scale control techniques and optimized timing.
- Enforcement of NO_x scrubbing technologies in smokestacks and stationary NO_x sources.
- Development of artificial wetlands around crop fields, acting as collectors of extra Nr.
- Control and abatement of Nr levels in wastewater and sewage

We have mentioned above that soil bacteria will nitrify ammonia to nitrate, which will accumulate in groundwater and agricultural runoff. The control of nitrate concentration[5] and the remediation of nitrate-rich wastewater has elicited great interest due to the suspect detrimental effect of high nitrate levels in drinkwater[2,3,8]: the *in vivo* conversion of this ion to nitrite raises concern because of the suspected toxicity of nitrite[1,4]. Usually, water remediation is performed with the technologically mature “active-sludge” microbiological process[6,7,9,10,29]. However, its drawback lies in the high energy requirements and the extensive production of sludge potentially harboring pathogens. Therefore, a widespread research has dealt with the development of effective (electro)catalytic processes for nitrate removal[11-13,30], mainly limited by the lack of product selectivity. Electrocatalysis, in particular, is a promising option: the energy required is fed as electrical energy, which can be supplied directly from wind farms or solar power plants. In addition, minimal input of extra chemicals is needed, in stark contrast to the fine balance of nutrients required by microorganisms for an efficient active sludge process. The chapters of this thesis will deal with fundamental aspects of the electrochemical remediation of nitrate-laden wastewater: the importance of the electrode material, pH and electrode potential on nitrite reduction, the selectivity-determining step of nitrate reduction. The following section will give a basic introduction of electrocatalysis and will be followed by a brief overview of the electrochemical behavior of the most important nitrogen-containing inorganic molecules.

1.2 Electrocatalysis

It is common to include electrocatalysis within the larger domain of heterogeneous catalysis[25], because the catalytic processes occur at the boundary between different phases: solid (the electrode), liquid (the electrolyte) and gaseous (reactants or products such as O_2 and H_2). However, other analogies with heterogeneous catalysis can be identified: for example, electrocatalysis is also based on an intimate interaction between the electrocatalyst surface and the reactant, and this interaction lies at the heart of the catalytic effect. It can be easily understood that the nature of the electrode material plays a fundamental role, just as the choice and the design of the catalytic active material in common heterogeneous catalysis. Moreover, the ability to control the electrode potential represents an additional degree of freedom of electrocatalysis, enabling a fine-tuning of the reaction selectivity or rates impossible for non-electrochemical conversions.

The hydrogen evolution reaction (HER) is a simple paradigmatic case. When this reaction is studied at a potential E far from the equilibrium potential E_{eq} of the reaction

$$2\mathrm{H}^{+} + 2\mathrm{e}^{-} \rightleftharpoons \mathrm{H}_2 \tag{8}$$

the current measured at the electrode, in the absence of mass limitations, is given by the Butler-Volmer equation[31], which, limited to a half-cell and converted into its logarithmic form, is known as the Tafel equation:

$$\eta = a + b \log I_0 \tag{9}$$

where $\eta = E - E_0$ is the *overpotential*. Obtaining a Tafel plot is a ubiquitous procedure in electrocatalytic research; the obtained b value, also known as Tafel slope, is a valuable indicator of the mechanism of the process involved. Commonly, reference is made to specific values of b which indicate that a particular mechanism is operative. Table 1 lists the most common Tafel slope values and the mechanistic schemes associated with each of them.

Abbreviation	***b* value (under standard conditions: *T* = 298 K and *α* = 0.5)**	**Full expression of *b***
$E^{‡}$	120 mV	$\frac{RT}{\alpha F}$
$EC^{‡}$	60 mV	$\frac{RT}{F}$
$EE^{‡}$	40 mV	$\frac{RT}{(1+\alpha)F}$
$EC^{2‡}$	30 mV	$\frac{RT}{2F}$

Table 1 List of “canonical” Tafel slope values, along with the mechanistic scheme associated with each of them and the full expression of *b* (for one-electron elementary steps).

where *E* stands for an electrochemical step and *C* is the abbreviation of a purely chemical step, ‡ indicates the rate-determining step, *α* is the “transfer coefficient”[31] (typically $\alpha \approx 0.5$ as mentioned in Table 1). In the literature concerning the electrocatalytic hydrogen evolution , the different elementary steps involved are the following three reactions. First,

$$H^{+} + e^{-} \longrightarrow H_{ads} \tag{10}$$

is known as the *Volmer reaction* (or “primary discharge”). An ensuing possible reaction is the “chemical recombination”, also known as *Tafel reaction*:

$$H_{ads} + H_{ads} \longrightarrow H_{2} \tag{11}$$

(which is a Langmuir-Hinshelwood reaction in surface-science terms), while another possible way of forming H_2 is the “electrochemical desorption”, shortly known as *Heyrovský reaction*:

$$H_{ads} + H^{+} + e^{-} \longrightarrow H_{2} \tag{12}$$

(which would be a Eley-Rideal reaction in the surface-science jargon).

The electrocatalyst primarily affects the exchange current I_0. The performance of various polycrystalline metal cathodes has been argued to follow a so-called volcano plot, where the exchange current I_0 is plotted as a function of the M-H bond strength[32]. The adsorption of atomic hydrogen is an intermediate step of reaction (8), as can be seen in reactions (10)-(12). Of course, the volcano plot is the translation of the Sabatier Principle[25] in electrochemical terms. Briefly, this principle states that the catalytic activity (plotted on the y axis as the reaction rate or a comparable parameter) of a class of catalysts towards a given reaction is qualitatively related to the interaction between one or more reaction intermediates and the catalytic material (plotted on the x axis as the enthalpy of adsorption or a related variable), and this trend graphically resembles a volcano (hence the name "volcano plot"). In other words, this is a rephrasing of the "golden mean": catalysts featuring an intermediate heat of adsorption will not be poisoned (contrary to materials having a high affinity to the reactants) but will still be able to bind the reactants strong enough for the reaction to occur (contrary to materials which interact with reactants too weakly).

Electrocatalysis lies at the heart of the contemporary renewed interest in electrochemistry. Energy production with fuel cells involves the electrocatalytic oxidation of a fuel (hydrogen or small alcohols) and usually the reduction of oxygen at the cathode; the latter reaction has elicited growing interest because new catalysts, possibly noble-metal free, are being investigated in order to decrease the overpotential required and therefore the energy losses of the process. On the other hand, electrocatalysis is also concerned with the conversion of small (polluting) molecules into valuable or harmless products. This is the case for two cathodic reactions: CO_2 reduction and NO_2^-/NO_3^- reduction, for which the issue of *selectivity* comes to the fore.

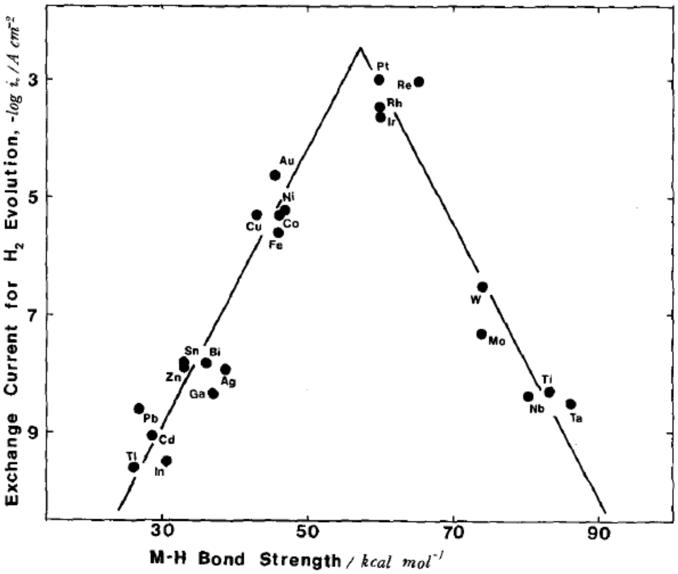


Figure 4 Exchange currents for electrolytic hydrogen evolution vs. strength of intermediate metal-hydrogen bond. From ref.31

1.3 Nitrogen cycle electrocatalysis

This section will briefly deal with the state of the art of the electrochemical investigation of simple nitrogen-containing inorganic molecules prior to this thesis. This background will help to appreciate the central role played by the nitrite ion, which is the main topic of the thesis, in the electrochemical nitrogen cycle. This chapter is a concise summary of literature information reported in more detail in our review that appeared in *Chemical Reviews* in 2009 [33]; therefore, it is meant as a practical reference summary for the interested reader.

An overview of the possible oxidation states of nitrogen compounds suggests that this cycle is characterized by a certain degree of complexity. Spanning from NH_3 to NO_3^-, the electrochemical nitrogen cycle can be summarized by a so-called oxidation state diagram, which plots the volt equivalent (VE, the standard potential times the nitrogen oxidation state) of the electrochemical equilibrium between a certain compound and N_2, versus the oxidation state of the compound. This is a powerful schematic representation which clearly shows that N_2 and NH_3 should be the thermodynamically most stable end-product of NO_3^- reduction. However, this graph neglects the kinetics of the reactions and the interaction with the solid-state catalysts that give rise to electrocatalysis. As a consequence, the actual catalytic reduction of nitrate usually gives rise to a host of products and few, if any, practical catalysts are able to attain 100% selectivity to N_2.

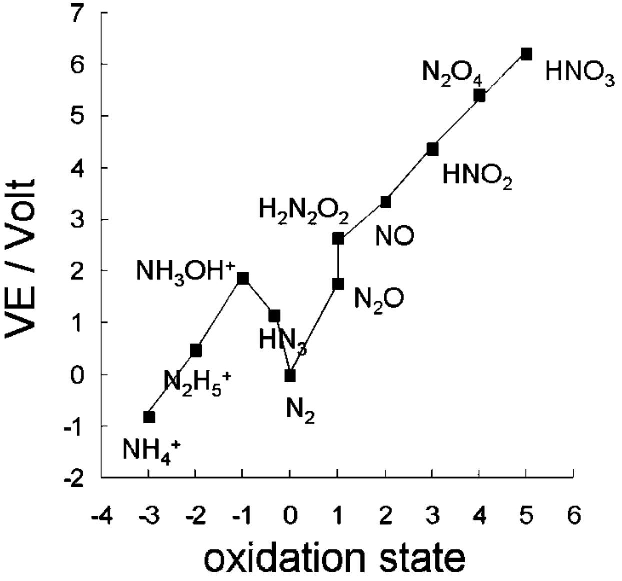
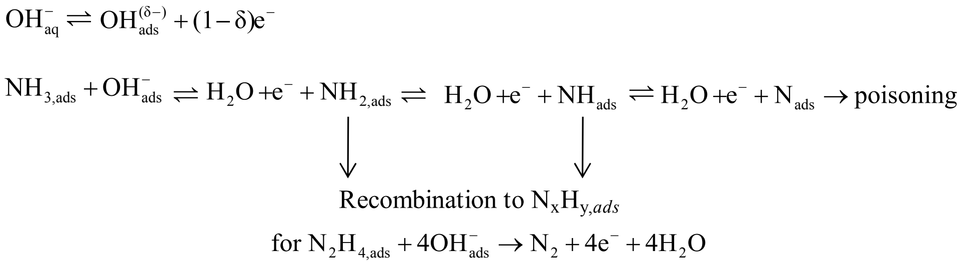


Figure 5 Oxidation state diagram for nitrogen-containing inorganic molecules

The following subsections will briefly deal with the electrochemical peculiarities of the individual molecules.

1.3.1 Ammonia

Ammonia is a possible product of nitrate/nitrite reduction, for example when electrode materials capable of breaking all N-O bonds of the nitrite molecule are chosen, such as rhodium (Chapter 6) or ruthenium (Chapter 7) . Ammonia oxidation has garnered much attention because this process could be used as anodic reaction in fuel cells. Most electrochemical research has employed polycrystalline platinum, whose electrocatalytic activity is maximum in alkaline media[34-40]. The most general mechanistic scheme, proposed by Gerischer and Mauerer[41],



$$OH^-_{aq} \rightleftharpoons OH^{(\delta-)}_{ads} + (1-\delta)e^-$$

$$NH_{3,ads} + OH^-_{ads} \rightleftharpoons H_2O + e^- + NH_{2,ads} \rightleftharpoons H_2O + e^- + NH_{ads} \rightleftharpoons H_2O + e^- + N_{ads} \rightarrow \text{poisoning}$$

$$\text{Recombination to } N_xH_{y,ads}$$

$$\text{for } N_2H_{4,ads} + 4OH^-_{ads} \rightarrow N_2 + 4e^- + 4H_2O$$

Figure 6 A schematic representation of the Gerischer-Mauerer mechanism, for $\delta = 0$

pointing out the poisoning role of N_{ads}, has been corroborated by later studies. Among more recent research, platinum single crystals (which appear in Chapters 3 and 4) were investigated by the Leiden[35] and Alicante groups[34,36,40]. The outstanding performance of Pt (100) was first described by Vidal-Iglesias et al.: this surface oxidizes NH_3 at potentials as low as 0.5 V, whereas other basal planes show little activity below 0.9 V[40], and selectively converts NH_3 to N_2[34]. The introduction of steps of (110) or (111) orientation in the Pt (100) surface is detrimental to the electrocatalytic activity of ammonia oxidation and suggests an extreme sensitivity of this reaction to the arrangement of square domains[36]. Similar results are discussed in Chapters 3 and 4 of this thesis, dealing with nitrite reduction in alkaline media at Pt (100) surfaces. Vidal-Iglesias et al. have also studied ammonia oxidation on shape-controlled nanoparticles, observing that "cubic" nanoparticles (i.e. nanoparticles featuring large (100) domains) are by far the most active[38]. Similarly, cubic nanoparticles discussed in Chapter 5 are characterized by a very large nitrite reduction activity in alkaline media. The details of the mechanism of ammonia oxidation on Pt (100) have been elucidated by Rosca and Koper, who have proposed the following scheme on the basis of spectroelectrochemical evidence[35]:

$$NH_{3,aq} \rightleftharpoons NH_{3,ads} \text{ (equilibrium)} \tag{13}$$

$$NH_{3,ads} + OH^- \rightleftharpoons NH_{2,ads} + e^- + H_2O \text{ (fast)} \tag{14}$$

$$2NH_{2,ads} \rightarrow N_2H_{4,ads} \text{ (rate-determining step)} \tag{15}$$

$$N_2H_{4,ads} \rightarrow \ldots \rightarrow N_2\,(\text{fast}) \qquad (16)$$

The stability of $NH_{2,ads}$ on Pt (100) above 0.33 V appears to be also one of the key prerequisites for the direct nitrite conversion to N_2 to occur (Chapters 3 and 4). The unusually high stability of $NH_{2,ads}$ on Pt (100) (with respect to other basal planes) surfaces has also been corroborated by DFT (Density Functional Theory) calculations[35,42,43].

1.3.2 Hydroxylamine

Hydroxylamine is the major product of the conversion of nitrite for various electrode materials: platinum, in acidic and alkaline media (Chapter 2), palladium (Chapter 7) and iron-protoporphyrin IX (a heme-containing molecule) immobilized on pyrolytic graphite (Chapter 8). In all these cases, the last N-O bond of nitrite cannot be broken by the electrocatalyst.

As an electroactive molecule, hydroxylamine can be both oxidized and reduced; in addition, it is fairly unstable and can be involved in various homogeneous-phase reactions such as its disproportionation,

$$4NH_3OH^+ \rightarrow 2NH_4^+ + N_2O + 2H^+ + 3H_2O \qquad (17)$$

its reaction with nitrous acid[44-46]

$$NH_3OH^+ + HNO_2 \rightarrow N_2O + H^+ + 2H_2O \qquad (18)$$

or its auto-oxidation in alkaline media[47].

Once more, platinum is the most studied electrocatalyst for the hydroxylamine redox reaction in acidic media, and it is one of the most active. For this reason, a Pt ring electrode was used in Chapters 2 and 7 to detect hydroxylamine generated at a disk electrode: however, reactions (17) and (18) can hamper hydroxylamine detection with a rotating ring-disk electrode, causing loss of hydroxylamine during transit from disk to ring (Chapter 2). Among other electrode materials, glassy carbon cannot adsorb hydroxylamine[48], while some electrocatalytic activity at gold electrodes has been recently reported in a spectroelectrochemical study by Godoi et al.[49].

A detailed study of hydroxylamine reactivity on platinum in acidic media was carried out by Rosca et al.[45,50,51], and a summary of their findings is shown in Figure 7. The interaction of hydroxylamine with the Pt surface is not particularly strong and the reactions of hydroxylamine are largely controlled by the coadsorption of more strongly adsorbed surface species (anions, intermediates, hydrogen). Therefore, hydroxylamine reduction will be inhibited by H_{upd}; hydroxylamine oxidation by the formation of intermediate NO_{ads}, which forms a stable adlayer in a broad potential region. Further oxidation to HNO_2 occurs above 0.8 V. It is indeed the presence of such adlayer that gives rise to the peculiar "loop" current at the ring electrode when hydroxylamine is detected (chapters 2, 7 and 8).

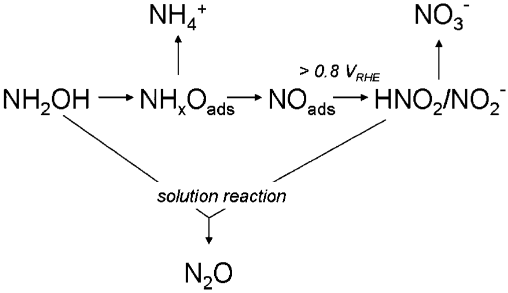


Figure 7 Mechanistic scheme of the electrocatalytic reactions hydroxylamine on platinum.

1.3.3 Nitrous oxide

Nitrous oxide is the main product of HNO_2 reduction on most noble metals, as will be shown in Chapters 2, 6 and 7. From the point of view of electrocatalysis, nitrous oxide is characterized by a reactivity limited to the following important reaction.

$$N_2O + 2H^+ + 2e^- \rightarrow N_2 + H_2O \tag{19}$$

Some materials reduce more oxidized nitrogen compounds to N_2O and finally produce N_2 (the ultimately desirable product) via reaction (19). However, in most cases the weakly-interacting N_2O escapes the electrode surface before the (sluggish) conversion to N_2 can take place: the coadsorption of all other species is detrimental to N_2O reduction. Although Pt (111) displays some reactivity towards nitrous oxide reduction, the most interesting metal is polycrystalline Pd, because it is active even in the presence of sulfate[52]. The mechanism also sets Pd apart from other metals, in that Attard et al.[52,53] have suggested that free Pd sites can decompose N_2O by adsorbing O at the surface:

$$N_2O_{ads} \rightarrow O_{ads} + N_2 \text{ slow irreversible reaction} \tag{20}$$

$$O_{ads} + 2H^+ + 2e^- \rightarrow H_2O \text{ fast reaction} \tag{21}$$

This mechanistic scheme is largely inspired to N_2O decomposition on metal surfaces (among which Pd(110)) under UHV(Ultra-High Vacuum)conditions[54].

1.3.4 Nitric oxide

Nitric oxide is central to this thesis, as it is for the nitrogen electrochemical cycle. Whenever nitrite reduction is studied in acidic media, NO_{aq} is released from nitrous acid decomposition and therefore the presence of NO_{aq} cannot be neglected[55,56]:

$$NO_2^- + H^+ \rightleftharpoons HNO_2 \qquad pK_a = 3.35 \tag{22}$$

$$2HNO_2 \rightleftharpoons NO + NO_2 + H_2O \tag{23}$$

$$3NO_2 + H_2O \rightleftharpoons NO + 2H^+ + 2NO_3^- \tag{24}$$

where stirring, gas flow or increased acidity enhance the decomposition by shifting the equilibrium to the right[57,58].

Two NO reduction experiments can be identified: NO adsorbed at an electrode surface, and continuous NO reduction (with NO in the solution). The adsorption of NO on metal surfaces has been widely studied in electrochemical and UHV systems and a distinction can be made between molecular or dissociative NO adsorption[59]. The electrocatalytic activity of transition metals towards nitrite reduction in acidic media will be interpreted in Chapter 7 with a volcano plot featuring the strength of adsorption of NO. Platinum offers a perfect example of a metal adsorbing NO molecularly and adsorption of NO under electrochemical conditions mirrors the observations of UHV studies. NO adlayers formed by exposure of Pt single-crystals[60,61] to a concentrated acidic nitrite solution can be removed by a single negative-going potential sweep (reductive stripping), with a complete recovery of the blank voltammetric profile. NO occupying different sites are reduced at different potentials and there is no clear catalytic effect of steps, in contrast to CO oxidative stripping[62,63]. All surface sites can dock NO and a coverage of 0.5-1 ML can be reached; NO_{ads} is converted to ammonia on all single-crystal surfaces provided that the coverage is low. When free sites available for the cleavage of the N-O bond are further occupied by NO_{ads} (corresponding to high coverage), hydroxylamine is the favored product. Other metals facilitate NO_{ads} dissociation[59] which, in turn, gives rise to the surface poisoning: N_{ads} fragments, in fact, are resilient and cannot be reduced and removed even with a low-sweep-rate potential scan, while this is always possible for molecularly adsorbed NO on Pt. This is the case for Rh(100) surfaces[64], polycrystalline Rh (Chapter 6), and single-crystal polycrystalline Ir[65-67] (Chapter 7). NO is also a well-known ligand of enzymes and some prosthetic groups, for example heme, feature a strong adsorption (NO effectively blocks the iron center). When heme is immobilized onto a carbon electrode, NO can be removed with a reductive stripping and hydroxylamine is released[68]. The affinity of heme to binding NO is central to nitrite reduction on hemin in acidic media (Chapter 8).

Continuous NO reduction takes place on all electrode systems mentioned above and features a peculiar reaction pathway for transition metals, different from the mechanism of NO stripping. The availability of NO_{aq}, along with the presence of NO_{ads} at most metal surfaces, gives rise to a recombination to a protonated NO dimer that dehydrates to N_2O[69,70]:

$$\mathrm{NO_{ads} + NO_{aq} + H^+ + e^- \rightarrow HN_2O_{2,ads}} \text{ rate-determining step} \tag{25}$$

$$\mathrm{HN_2O_{2,ads} + H^+ + e^- \rightarrow N_2O + H_2O} \text{ fast} \tag{26}$$

Stable NO dimers have been detected on Ag[71,72], in particular. The heme group can perform continuous NO reduction as well, but the selectivity of the reduction is dependent on the pH[73]:

$$\mathrm{NH_3OH^+} \xleftarrow{pH<5} \mathrm{NO} \xrightarrow{pH>10} \mathrm{N_2O} \tag{27}$$

A general scheme summarizing NO reduction at metal electrodes can be found in Figure 8:

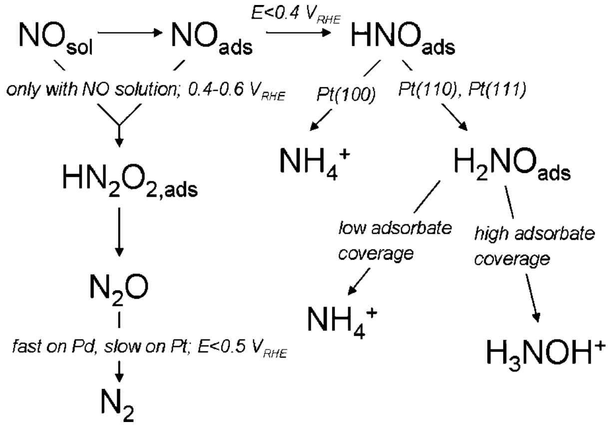


Figure 8 Summary of the main electrochemical reduction reactions of NO on transition metals.

1.3.5 Nitrite

Nitrite reduction is the key topic of this thesis; the rich homogeneous-phase chemistry of nitrite has been outlined above in the sections dealing with hydroxylamine and nitric oxide; more generally, the study of nitrite reduction is of paramount importance because it is the selectivity-determining step of nitrate reduction.

The literature focused on nitrite electrochemistry is relatively scarce. In acidic media, a distinction between the electrochemistry of dissolved NO and direct HNO_2 reduction must be made. Gadde and Bruckenstein[74] were the first to report a direct diffusion-controlled conversion of HNO_2 to NH_3OH^+ at a rotating Pt electrode in acidic media. Among other metals, usually acidic nitrite solutions are used to generate NO adlayers which can be studies with spectroelectrochemical techniques; the research has focused on Rh[64] (see Chapter 6), Pd[75] and Ru[76] (see Chapter 7).

Much less research has dealt with nitrite reduction in neutral or alkaline solutions: under these conditions the reduction of the nitrite ion has often been reported to be fairly sluggish. The most interesting study, which partly inspired Chapter 3, was published by Ye et al.[77,78] and described the reaction order of the Pt single-crystal basal planes towards nitrite reduction in alkaline media: Pt(100)>>Pt(110)>Pt(111). Pt(100) was shown to convert nitrite mainly to ammonia. This product could be reoxidized at Pt(100) to give N_2 in the subsequent positive-going anodic scan.

Nitrite reductases are widespread enzymes and they owe their *in vivo* activity to a tertiary structure which facilitates the docking of nitrite via specific aminoacid side groups. This is also true for NO-binding proteins such as myoglobin or hemoglobin[21,79-82]. When a whole protein is immobilized (for example myoglobin or hemoglobin[83]) the nitrite reduction catalytic activity is conserved and electrochemical nitrite reduction at pH 7 can be performed.

1.3.6 Nitrate

Nitrate, as has been stated above, is the ubiquitous form of Nr pollution of ground- and wastewater. Therefore, many studies have investigated the performance of various cathodes for the removal of this ion, mainly in acidic media and low nitrate concentrations (< 1 M). Under these conditions, the mechanism operative for polycrystalline metals was studied by Dima et al.[84]: the first electron transfer is the rate-determining step, as evidenced by a Tafel slope of 120 mV.

$$\mathrm{NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O} \text{ rate-determining step} \qquad (28)$$

A stepwise conversion of nitrite via NO to NH_4^+ will then take place. Dima et al. have also shown that the electrocatalytic activity for nitrate reduction decreases along the order Rh > Ru > Ir > Pt ~ Pd for transition metals, and Cu > Ag > Au for coinage metals, when the reaction is carried out in H_2SO_4. The importance of the anion of the supporting electrolyte must be stressed: nitrate reduction on Pt, for example, is heavily hindered by the coadsorption of bisulfate, as well as other anions[85,86]. In addition, nitrate reduction at Pt electrodes, also in the absence of strongly interfering anions (i.e. in $HClO_4$), is typically characterized by a drop in reduction current in the hydrogen UPD region: in fact, it has been shown[87,88] that even adsorbed hydrogen can interfere with the weakly adsorbed nitrate ion, which is thought to adsorb in a chelating bidentate configuration[89]. The key to the high electrocatalytic activity of Rh is the large affinity to anion adsorption, which unfortunately also gives rise to the often undesired perchlorate reduction[90]. The study of nitrate reduction at Pt single-crystals[91-93] has largely corroborated the mechanistic picture outlined above, with the exception of Pt (110), which is the most active surface in $HClO_4$. For this basal plane, a Tafel slope of 60 mV was found[92],which corresponds to the following mechanistic scheme:

$$NO_3^- \rightleftharpoons NO_{3,ads}^- \tag{29}$$

$$H^+ + e^- \rightleftharpoons H_{ads,nt} \tag{30}$$

$$H_{ads,nt} + NO_{3,ads}^- \rightarrow \ldots \text{ rate-determining step} \tag{31}$$

H_{nt} is hydrogen adsorbed on the narrow terraces (of reconstructed Pt (110)) at high potential. When $HClO_4$ is used, steps are beneficial to the catalytic activity, and Dima et al. have presented some evidence of NO accumulation at steps[91]. Hydrogen adsorbed at (110) sites at low potentials (H_s, hydrogen at “steps”) is on the other hand responsible for the inhibition of nitrate reduction.

Given the sluggishness of nitrate reduction at Pt, various bimetallic systems have been studied in order to enhance the catalytic activity and steer the selectivity to N_2, or NH_3OH^+ (a valuable industrial product). PtCu electrodes, for example, show an enhanced nitrate reduction activity, although NH_3 is still the main product[94]. Electrocatalysis by ad-atoms is another possibility and PtSn is one of the most studied combinations[95-98]: it has been shown that an intermediate Sn coverage (0.4 ML) is optimal and greatly enhances the nitrate reduction current. Recently, the influence of the Sn coverage on the reaction selectivity has been reported[99]: N_2O is the predominant product at intermediate Sn coverages, while NO is the main product for higher Sn coverage. Claims of remarkable increases in N_2 evolution (up to 30%) during long-term electrolysis[95-98] have been recently questioned, in the light of the complex homogeneous-phase reactions that may take place among products in the solution[99]. Sn is supposed to supply highly oxophilic sites that facilitate the breaking of the N-O bond during the conversion of nitrate to nitrite, which is however still the rate-determining step.

Finally, the bimetallic combination PdCu has emerged as one of the most promising, since the catalytic activity of Cu can be paired to the N_2O reduction activity peculiar to Pd. De Vooys et al. have shown that a low copper coverage on Pd achieves a N_2 selectivity of ca. 40%[100].

1.4 Outline of this thesis.

The aim of this thesis is essentially twofold: on the one hand, a fundamental investigation of the mechanistic details of nitrite reduction as a function of electrode material and pH has been carried out (Chapters 2,6,7,8); on the other hand, we delved into the direct reduction of nitrite to N_2 at Pt(100) domains in alkaline media, with an eye to establishing the structure-sensitivity of this reaction, which was then used as a characterization tool for preferentially-oriented Pt nanoparticles (Chapters 3,4 and 5).

The research began by reinvestigating the peculiarities of polycrystalline Pt through evaluating the role of dissolved and adsorbed NO during HNO_2 reduction (Chapter 2) and continued with the study of another metal that adsorbs NO molecularly, Rh (Chapter 6). Rh, in contrast with Pt, is able to cleave the N-O bond and the selectivity of the nitrous acid reduction at low potentials shifts from hydroxylamine to ammonia accordingly. We then extended the investigation of nitrite/nitrous acid reduction to the most important remaining polycrystalline transition metals, highlighting the validity of the Sabatier Principle for the interpretation of the electrocatalytic activity towards nitrite/nitrous acid reduction. An intermediate metal-NO adsorption energy is optimal; those metals that bind NO too strongly, or even dissociate it, can become poisoned by its fragments (Ir, Ru), while coinage metals (Au, Ag, Cu) tend to adsorb NO too weakly (Chapter 7). Finally, the mechanism of nitrous acid reduction at a biologically relevant moiety (protoporphyrin IX) was studied, evidencing the central role of NO ligation to the iron center of the heme group for the electrocatalytic conversion (Chapter 8).

The central chapters of the thesis focus on the most exciting discovery of the entire project: Pt(100) was found to be able to convert nitrite to N_2 in alkaline media with a high selectivity, in contrast to the poor catalytic activity of other Pt basal planes (Chapter 3). The molecular underpinnings of direct nitrite reduction at Pt(100) in alkaline media were then investigated (Chapter 4). Experimental evidence supported a mechanism akin to two other well-known pathways leading to N_2: microbial "anammox"[101,102] (anaerobic ammonia oxidation: $NO_2^- + NH_3$) and the selective-catalytic reduction NO + NH_3 at Pt(100) surfaces in UHV[103-106]. Consequently, a particular type of practical catalysts, i.e. Pt nanoparticles with preferential (100) orientation[107], will be analyzed in Chapter 5. Since nitrite reduction at Pt(100) is sensitive to the long-range orders of (100) domains (Chapter

4), this reaction was also used as ancillary characterization reaction[108] for platinum nano-cubes, along with dimethylether oxidation[109,110], ammonia oxidation[36,38,40] and CO stripping[107]. The most ordered cubic nanoparticles obtained with the new "cathodic corrosion"[111] method showed the expected N_2 evolution and could hopefully serve as practical catalysts for real nitrite removal applications.

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