Interconversions of nitrogen-containing species on Pt(100) and Pt(111) electrodes in acidic solutions containing nitrate

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This work deals with the interconversions of various nitrogen-containing compounds on Pt(111) and Pt(100) electrodes in contact with acidic solutions of nitrate. Via its reduction, nitrate acts merely as the source of adsorbed nitrogen-containing intermediates, which then undergo complex oxidative or reductive transformations depending on the electrode potential. Nitrate reduction to ammonium is structure sensitive on Pt(111) and Pt(100) because it is mediated by NO, the adsorption and reactivity of which is also structure sensitive. Accordingly, previous knowledge from NO electrochemistry is useful to streamline nitrate reduction and elaborate a comprehensive picture of nitrogen-cycle electrocatalysis. Our overall conclusion for nitrate reduction is that the complete conversion to ammonium under prolonged electrolysis is possible only if the reduction of nitrate to nitric oxide, and the reduction of nitric oxide to ammonium are feasible at the applied potential. Among the two surfaces studied here, this condition is fulfilled by Pt(111) in a narrow potential region.

1. Introduction

Electrochemical reactions involving nitrogen-containing compounds have been traditionally attractive to understand fundamentals of electrochemical surface science and electrode kinetics [1–3]. Such reactions include (but are not limited to) nitrate reduction, nitric oxide reduction or oxidation [4,5], nitrous oxide reduction [6,7] or ammonia oxidation [8,9]. Apart from their fundamental importance, some of the above reactions may additionally have potential applications in the fields of wastewater treatment [10–12], electrochemical sensors [13], electrochemical synthesis [14], and energy conversion [15]. Overall, the reactions of nitrogen-containing compounds are complicated, as they typically involve several bond-breaking or bong-forming events and thus several intermediates and final products are formed. These processes are in fact interconnected within the biogeochemical nitrogen cycle and often share the same intermediates [16].

The reduction of nitrate exemplifies the complexity of the electrocatalysis of the nitrogen cycle. This reaction has been investigated on several monometallic [17–23], bimetallic [23–26] or modified [3,27–30] electrodes in which various final products such as nitrite, NO, N₂O, N₂, NH₂OH or NH₃ can be formed. Platinum single-crystal electrodes have also been utilized to understand structural effects on the reactivity and product distribution [2,31–34].

Herein, we study the voltammetric and spectroscopic behaviour of Pt(111) and Pt(100) electrodes in acidic solutions containing nitrate. Our focus is placed on the formation of adsorbed intermediates and desorbed products as a function of the electrode potential. We use classical electrochemical techniques, vibrational spectroscopy as well as density functional theory (DFT) calculations. We show that adsorbed nitrogen-containing species that originate from nitrate reduction undergo complex, potential-driven transformations which are structure sensitive. The electrochemical behaviour is eventually controlled by the reactivity of these...
adsorbates and nitrate in solution merely provides the surface with such adsorbates. Therefore it is anticipated that the findings of this study can be extended to other electrocatalytic reactions relevant to the nitrogen cycle which form the same intermediate species.

2. Experimental methods

The electrochemical measurements were performed in a glass electrochemical cell. The working electrodes were Pt beads (Prof. Juan Feliú, University of Alicante) in the hanging meniscus configuration. Prior to each measurement, the crystal was flame-annealed and cooled to room temperature in an Ar:H₂ (3:1) environment, in accordance to a well-established methodology [35,36]. The clean, well-ordered single-crystal electrode was immersed in the solution at +0.07 V_RHE, unless otherwise stated. The voltammograms always represent the first cycle after annealing, starting from −0.07 V_RHE to the positive direction, unless otherwise stated. The counter electrode was a Pt wire, also flame-annealed before the measurement, and the reference was a reversible hydrogen electrode (RHE).

The Fourier transform infrared spectroscopy experiments were performed with a Bruker Vertex 80v vacuum spectrometer in the external reflection mode, using an MCT detector and p-polarization, in the thin-layer configuration using a spectroelectrochemical cell similar to the one described previously [37]. The working electrode for these measurements was a platinum single-crystal disk from Mateck GmbH, prepared as described for the Pt beads in the previous paragraph. Each spectrum represents the average of 100 interferograms collected with a resolution of 8 cm⁻¹. The spectra were intentionally recorded under potentiostatic conditions to allow a high signal-to-noise ratio while being at a steady state. The spectra are shown as (R−R₀)/R₀, where R and R₀ are the reflectance at the sample and reference potential, respectively. Therefore, positive bands correspond to species in excess at the sample potential with respect to the reference potential and negative bands to species in deficiency at the sample potential with respect to the reference potential.

“Online” ion chromatography was performed in accordance to the methodology described by Yang et al. [38]. The methodology for the formation of NO adlayers and subsequent reductive stripping has been described previously [5].

An Autolab PGSTAT302 N potentiostat was used for the potential control and the current measurement. Compensation for the electrolyte resistance was done with positive feedback. The measurements were performed at room temperature in an electrolyte saturated with Argon. The current was normalized to the geometric area of the working electrode.

The electrolyte was always freshly prepared using ultrapure water (Merck Millipore, 18.2 MΩ, TOC < 3 ppb) and concentrated perchloric acid (Merck Suprapur, 70%). The gases used were 6 N quality (Airgas Inc.). All glassware was cleaned in an acidic solution of potassium permanganate overnight, followed by rinsing with an acidic solution of hydrogen peroxide and repetitive rinsing and boiling with ultrapure water.

Computationally, the free energy was approximated as: 

\[ G = E_{DFT} + ZPE - TS + E_{solution} \]

The DFT total energies (E_DFT), zero-point energies (ZPE) and entropy terms (TS) of ‘N’, ‘NH’, ‘NHO’, ‘NOH’ and ‘NO’ at Pt(100) were taken from a previous study [5]. The solvation corrections (E_solution) were taken from the work of Greeley and co-workers [39] and the energy of protons and electrons was assessed by means of the computational hydrogen electrode [40], which allows reporting the adsorption energies in Fig. 6 at a potential of 0.75 V. Note that the calculated adsorption energies in Fig. 6 use a different reference with respect to previous studies: here we consider as a reference the reactants of the elementary step under consideration.

3. Results and discussion

3.1. Nitrate reduction on Pt(111)

The voltammograms in 0.1 M HClO₄ solutions with and without nitrate on Pt(111) are shown in Fig. 1 (solid and dotted curve, respectively). The “blank” (nitrate-free) voltammogram exhibits the typical features of a well-ordered Pt(111) electrode in this solution [36]. When scanning from +0.07 V_RHE in the positive direction (solid black curve), nitrate reduction starts above +0.25 V_RHE (R111), following desorption of hydrogen, which inhibits the reaction at less positive potentials. The reductive current is maximized at +0.35 V_RHE and then decreases, probably because intermediates of nitrate reduction remain adsorbed and are not further reduced. The complete suppression of the “OH-related” “butterfly” features at ca. +0.8 V_RHE [36] indicates that such blocking species are not only stable between ca. +0.45 to +0.85 V_RHE but also detrimental for “OH adsorption.

In the reverse scan (solid gray curve in Fig. 1), significant processes are observed again only below +0.45 V_RHE with two reductive waves centered at ca. +0.32 V_RHE (R111) and ca. +0.1 V_RHE (R111). The voltammetric profile resembles the reductive NO stripping from Pt(111) (red dashed curve for a full NO layer, shown for comparison) [5]. Thus, we attribute R111 and R111 to the reduction of NO formed from nitrate reduction during the positive-going scan. Besides, NO is the species responsible for the suppression of the “butterfly” features. The two waves are related to the reduction of NO adsorbed at on-top (R111) and fcc-hollow (R111) sites [41]. From the comparison of the charge densities in nitrate-containing solution and in the Pt(111)-NO layer for each peak (i.e. compare solid gray and dashed red curve for both peaks), we conclude that the NO formed from nitrate reduction is nearly at saturation on the fcc-hollow sites while the coverage on the top sites is significantly lower. The preference of the formed NO for the fcc-hollow sites is related to the fact that this is the most stable
adsorption site for *NO on Pt(111), followed by atop *NO [5]. Therefore, the surface blockage observed during a potential cycle occurs because nitrate reduction forms the blocking species (*NO on the fcc-hollow site) at a potential where *NO is stable and requires a more negative potential for its reduction.

We recorded the FTIR spectra at different potentials in the nitrate-containing solution (see Fig. S1 in the Supporting Information, SI) but did not observe any band for NO in the entire potential region. This is reasonable because the N=O stretching from *NO on the fcc-hollow site is known to have a very low intensity, while atop *NO, which can be observed with infrared spectroscopy, has a low coverage here from nitrate reduction [5]. Remarkably, a positive band was observed at ca. 2343 cm⁻¹ for a potential step from −0.4 to +0.85 VRHE (Fig. S1). We assign this band to hyponitrous acid (HON=NOH), based on the transmission spectrum recorded in a 0.1 M HClO₄ + 0.01 M trans-Na₂N₂O₂ solution (Fig. S2). The conjugate base of hyponitrous acid, the hyponitrite ion (N₂O₃⁻) has previously been identified as an intermediate of nitrate reduction on tin, in alkaline solution [22]. The detection of H₂N₂O₂ here is a strong evidence of nitrate reduction via *NOH, i.e. the precursor of hyponitrous acid [42].

3.2. Nitrate reduction on Pt(100)

Similar to Pt(111), the reduction of nitrate on Pt(100) commences only after hydrogen desorption at ca. +0.3 VRHE, as concluded by comparison between the voltammograms in nitrate-free (dotted curve) and nitrate-containing solutions (solid curve) in Fig. 2. The reduction reaction is associated with a very sharp peak (R¹⁰⁰) at ca. +0.34 VRHE in the positive-going scan. The introduction of only a small density of (110) steps on Pt(100) is detrimental for the intensity of the R¹⁰⁰ peak, suggesting that the reduction of nitrate in the region of the sharp peak takes place predominantly on (100) terraces (see Fig. S3 for Pt(10 1 0)). In addition, the R¹⁰⁰ peak current density scales linearly with the scan rate (in the range 1−50 mVs⁻¹) which implies that the current is controlled by a surface process (see Fig. S4a).

The FTIR spectra in H₂O and D₂O (Fig. 3a and b, respectively) for a potential step from Ereference = +0.2 V to Esample = +0.4 V (spectra in red) show only a strong negative band at ca. 1360 cm⁻¹ attributed to the depletion of nitrate during this potential step. We did not observe any NH₄⁺ characteristic band at ca. 1460 cm⁻¹ in H₂O, between +0.2 and +0.4 VRHE, while “online” chromatography did not provide any evidence that ammonium forms during the R¹⁰⁰ peak, either. In addition, if the potential scan is limited between +0.3 and +0.4 VRHE, the otherwise sharp R¹⁰⁰ disappears already from the second scan (see Fig. S5). The above observations indicate that ammonium is not a major product of the reduction of nitrate in the R¹⁰⁰ peak, but instead the reduction is accompanied with the adsorption of inactive nitrogen-containing intermediates that suppress the reaction.

In the potential region from +0.4 to +0.65 VRHE (still in the positive-going scan) the reaction takes place with a low rate, as seen in the voltammogram in Fig. 2 where a small reduction current is recorded. This corroborates with the spectra at Esample = +0.65 V with Ereference = +0.4 V in H₂O and D₂O (Fig. 3, spectra in green) which show the formation of products of nitrate reduction. In particular, the spectrum in Fig. 3a (i.e. in H₂O) shows a positive band at 2343 cm⁻¹ assigned to H₂N₂O₂, which again indicates that *NOH forms as the precursor of hyponitrous acid. In addition, a positive band is observed at 1570 cm⁻¹ in Fig. 3b (i.e. in D₂O) and is assigned to low-coverage *NO adsorbed on bridge sites [5]. The origin of *NO is probably from the HNO₂ produced by nitrate reduction, as HNO₂ is known to disproportionate in acidic solution.

While on Pt(111) *NO is reduced at more negative potentials than nitrate, on Pt(100) low-coverage *NO can be reduced in the potential region of nitrate reduction, via *NHO, *N and *NHₓ as shown previously [5]. Since we detect *NO in this potential region with the infrared measurements, it is likely that such *NO partially undergoes reduction to any of the above species.

A further increase of the potential in the voltammetry leads to an oxidative peak centered at +0.75 VRHE (Fig. 2). The peak current is linearly dependent on the scan rate which points to a surface-confined process (Fig. S4b). In the infrared spectra, an asymmetric bipolar band is observed at +0.85 VRHE in D₂O (with reference at +0.65 V, spectrum in cyan in Fig. 3b), with a small negative component at ca. 1570 cm⁻¹ and a large positive
component at ca. 1610 cm$^{-1}$. The shift of the NO band from 1570 to 1610 cm$^{-1}$ as well as the asymmetric character of the bipolar band are clear indications that $^{*}$NO coverage increased substantially from +0.65 V to +0.85 V [5]. The increase in $^{*}$NO coverage during the O$^{100}$ peak is significant enough to observe a positive band at 1610 cm$^{-1}$ even in H$_2$O (Fig. 3a, spectrum in cyan) where $^{*}$NO detection is typically more difficult because of interference from water bands [5].

The reaction that leads to $^{*}$NO formation during the O$^{100}$ peak involves the oxidation of a nitrogen-containing adsorbate, hereafter denoted N$_3$H$_4$O$_2$, which forms previously from nitrate reduction (i.e. at any potential before the O$^{100}$ peak). The oxidation state of nitrogen in N$_3$H$_4$O$_2$ is lower than +2, because $^{*}$NO is a product of the oxidation of N$_3$H$_4$O$_2$. When nitrate concentration increases in solution, it is likely that its reduction results in higher $^{*}$NO coverage. From a previous study, we showed that $^{*}$NO is more stable towards reduction to $^{*}$NHO on Pt(100) when its coverage is lower [5]. Here, we find that the O$^{100}$ peak diminishes by increasing the nitrate concentration (see Fig. 4). A reasonable interpretation of this observation is that the more compact and more stable $^{*}$NO adlayer from the reduction of nitrate at higher concentrations is detrimental for the formation of N$_3$H$_4$O$_2$, e.g. because $^{*}$NO reduction is inhibited when $^{*}$NO coverage increases. Considering that the product of $^{*}$NO reduction at low coverages is $^{*}$NHO [5], a likely candidate for N$_3$H$_4$O$_2$ is $^{*}$NHO.

Apart from $^{*}$NO, H$_2$N$_2$O$_2$ is again observed with a band at 2343 cm$^{-1}$ in the potential step from +0.65 V to +0.85 V, which suggests that hyponitrous acid is still formed above +0.65 V$_{RHE}$ (Fig. 3a, spectrum in cyan).

During the negative-going scan (solid gray curve in Fig. 2), a small reductive peak is observed at +0.735 V$_{RHE}$ (R$^{100}$). The infrared spectroscopy at +0.65 V$_{RHE}$ (reference at +0.85 V$_{RHE}$) shows a bipolar band for $^{*}$NO, mainly due to the Stark effect (Fig. 3b, spectrum in blue). When the crystal was immersed in nitrate solution at +0.85 V$_{RHE}$ immediately after annealing in a separate experiment, i.e. without prior reduction of nitrate at lower potentials and subsequent adsorption of any reaction products, we observed the following: (i) the R$^{100}$ peak was much more pronounced compared to the experiment in Fig. 2a (Fig. 5); (ii) NO formation was observed during the step from +0.85 V to +0.65 V by infrared spectroscopy (inset a in Fig. 5); (iii) the R$^{100}$ peak current is linearly dependent on the scan rate (inset b in Fig. 5); and (iv) the peak position depends on the logarithm of the concentration of nitrate in solution (inset c in Fig. 5). Based on all of the above, we assign the R$^{100}$ peak to the reduction of nitrate to $^{*}$NO, in agreement with a previous hypothesis [34]. This proposition is consistent with the standard potential of the HNO$_3$(l)/NO(g) couple (+0.957 V$_{RHE}$) which must be even more positive for the HNO$_3$(l)/NO couple considering the strongly exothermic adsorption of NO on Pt(100).

The reduction of nitrate to $^{*}$NO during the R$^{100}$ peak takes place on platinum sites that were not available before the O$^{100}$ peak. Otherwise, the reaction would have already taken place at the more favoring lower potentials during the positive-going scan. The increased site availability after the O$^{100}$ peak reveals that the N$_3$H$_4$O$_2$ species occupies more platinum atoms than the produced $^{*}$NO, so the N$_3$H$_4$O$_2$ oxidation to $^{*}$NO results in unoccupied Pt sites which are free for nitrate reduction to $^{*}$NO in the negative-going scan. This claim is also supported by the fact that the R$^{100}$ peak diminishes by increasing the HNO$_3$ concentration (see Fig. 4), as higher nitrate concentrations lead to higher $^{*}$NO coverage already from nitrate reduction in the positive-going scan, as mentioned already above, at the expense of other nitrogen-containing compounds.

Previous electronic-structure calculations showed that at low and relatively high coverage, $^{*}$NO is a bridged adsorbate on Pt(100), so that each $^{*}$NO occupies two Pt atoms [5]. In an attempt to determine the exact composition and structure of N$_3$H$_4$O$_2$, we observe that the only nitrogen-containing adsorbates with nitrogen at an oxidation state lower than +2 and with higher occupancy than two surface Pt atoms are $^{*}$NHO, $^{*}$N and $^{*}$NH. Note in passing that all of these three species adsorb on 4-fold hollow sites on Pt(100).

Fig. 5. Cyclic voltammetry (5 mV s$^{-1}$) on Pt(100) in 0.1 M HClO$_4$ + 0.001 M NaNO$_3$, starting from +0.70 V$_{RHE}$ (dotted curve) or from +0.85 V$_{RHE}$ (solid curve). Inset (a): Infrared spectrum at +0.65 V$_{RHE}$ with the reference potential at +0.85 V$_{RHE}$ for a solution of 0.01 M NaNO$_3$, when the contact of the annealed electrode with the solution was done at +0.85 V$_{RHE}$. Inset (b): Scan rate dependence of the peak current for nitrate reduction when the measurement started from +0.85 V$_{RHE}$. Inset (c): Concentration dependence of the peak potential for nitrate reduction when the measurement started from +0.85 V$_{RHE}$.

Fig. 4. Cyclic voltammetry (5 mV s$^{-1}$) on Pt(100) in 0.1 M HClO$_4$ with different concentrations of nitrate. The arrows are used as a guide to the eye for the dependence of the O$_1$, R$_2$, and R$_3$ peaks as the concentration of nitrate increases.
Assuming that *NHO, *N and *NH are present at the surface at +0.75 V_{RHE} and that only downhill elementary steps are thermodynamically feasible at such potential, we evaluate the most favorable way of oxidizing them to *NO by means of electrochemical steps (see the details of the calculations in the Experimental methods section). According to Fig. 6, the oxidation of *NHO to *NO is entirely exothermic at +0.75 V_{RHE}, a representative potential of the O1_{100} peak in Fig. 2. Conversely, the oxidation of either *N or *NH to *NO involves at least one endothermic step. Therefore, we propose that the *NxHzOy adsorbate oxidized to *NO at the O1_{100} peak is *NHO, most likely formed via *NO hydrogenation below ca. +0.6 V_{RHE}. This proposition is in agreement with the interpretation made above for the concentration dependence of the O1_{100} peak.

In the potential region from +0.65 to +0.4 V_{RHE} in the negative-going scan a reduction wave (R1_{100}) is observed in Fig. 2, and the infrared spectra in either H2O or D2O for the same potential region show unambiguously that the peak R1_{100} is associated to the reduction of *NO (see negative band in Fig. 3a and b, spectrum in pink). The potential at which *NO is reduced here is more positive by ca. 250 mV than the potential in which a full *NO adlayer is reduced [43]. This is because the onset potential for *NO reduction at low coverage is more positive than for a saturated *NO adlayer, as also mentioned above [5]. For instance, the red dashed curve in Fig. 2 shows the response for the reduction of a partial Pt(100)-*NO layer in a clean (nitrate-free) solution. The increase in the concentration of nitrate leads to a shift in the position of R1_{100} toward more negative potentials (see Fig. 4), which is an indication of higher *NO coverage by increasing nitrate concentration. The reduction of *NO at the R1_{100} peak yields mainly a nitrogen-containing adsorbate: this is evident by the infrared spectra that show *NO depletion for the step from E_{reference} = +0.65 V to E_{sample} = +0.4 V, though without a significant positive band for NH4+ (Fig. 3a, spectrum in pink).

Based on our previous conclusion that low-coverage *NO is reduced via *NHO [5], we hypothesize that the *NO formed is subsequently reduced to *NHO at the R1_{100} peak. To prove this hypothesis, in separate experiments we restricted the low-potential limit (LPL) within the R1_{100} region. Indeed, we found that the processes in the O1_{100} and R1_{100} peak are strongly connected: by using a more positive LPL (e.g. blue curve in Fig. 7) the charge for the O1_{100} peak decreases. Therefore, we conclude that in the R1_{100} peak *NO is reduced to *NHO, which is oxidized back to *NO in the O1_{100} if the scan is reversed as in the measurements in Fig. 7.

Returning to Fig. 2, the surface is free from nitrogen-containing adsorbates in the negative-going scan, only at potentials below +0.4 V_{RHE}. A reductive process takes place at potentials around +0.2 V_{RHE}, and the infrared spectra show the formation of dissolved ammonium (see positive band at 1460 cm\(^{-1}\) in H2O for the step from +0.4 V to +0.2 V, Fig. 3a, spectrum in gray).

3.3. Proposed mechanism

We propose here a scheme (Scheme 1) summarizing the structure-sensitive transformations of nitrogen-containing species.

![image](image-url)
generated on single-crystal Pt(111) and Pt(100) from acidic nitrate solutions as described in the previous sections.

On both Pt(111) and Pt(100) the reaction starts from the deoxygenation (hydrogenation) of HNO₃ to HNO₂ once hydrogen desorption takes place, i.e. above ca. +0.25 to +0.3 V depending on the surface facet. In acidic solutions, HNO₂ disproportionates to HNO₃ and NO and the former is exothermically adsorbed on the Pt surfaces. The detection of hyponitrous acid in infrared spectroscopy on both facets indicates that in parallel with HNO₂ disproportionation, further deoxygenation of HNO₂ to *NOH and dimerization to H₂N₂O₂ takes place.

The reaction steps described so far are identical for Pt(111) and Pt(100), but the pathways diverge once adsorbed *NO is formed as a result of the structure-sensitive reduction of *NO [5]. On Pt(111), *NO adsorbed on top sites can be reduced to *NOH only below +0.4 V, while *NO adsorbed on the fcc-hollow sites is reduced at even less positive potentials (below +0.25 V).

In contrast, on Pt(100) *NO is reduced to *NHO at potentials below +0.60 V as long as the *NO layer is not saturated. *NHO is reduced to NH₄⁺ at a less positive potential (below ca. +0.4 V) and oxidized to *NO at ca. +0.75 V. Therefore, once *NHO is formed from *NO during a potential sweep in the region from ca. +0.4 to +0.6 V, it will be oxidized or reduced depending on the direction of the scan, at suitable potentials. This implies that the complex behaviour of acidic nitrate solutions on Pt(100) is not a result of nitrate reactivity itself, but of the peculiar behaviour of *NO on this surface facet.

Scheme 1 also explains additional observations for Pt(100) described in the Results section. For example, the complex relationship between the O₁₀₀, R₁₀₀ and R₁₀₀ shown in Fig. 2 is understood by the higher site occupancy of *NHO compared to *NO on Pt(100). During the O₁₀₀ peak, the dehydrogenation of *NHO releases platinum sites which are then free to reduce HNO₃ to *NO in the R₁₀₀ peak in the reverse scan. By lowering the potential further, *NO is reduced to *NHO in the R₁₀₀ peak. The charge of the O₁₀₀ and R₁₀₀ peaks depends on the coverage of the previously formed *NHO; a low coverage of *NHO (for example in more concentrated nitrate solutions) will result in a lower current for the *NHO to *NO oxidation (O₁₀₀ peak), and thus less free Pt sites for the reduction on HNO₃ to *NO (R₁₀₀ peak).

Based on this discussion, we conclude that the complete conversion of nitrate to ammonium on platinum is determined by the reduction of adsorbed NO, which otherwise acts as a poison. For both Pt(111) and Pt(100), *NO is reduced to NH₄⁺ in a more negative potential region compared to nitrate reduction to *NO. Under potentiostatic conditions, we anticipate that the complete reduction of nitrate to ammonium is possible only in the potential region where both reactions can take place. From the data shown in Figs. 1 and 2, this condition is fulfilled only by Pt(111), at potentials from ca. +0.25 V to +0.4 V.

4. Conclusions

We summarize below the main findings of our study on the reduction of nitrate in acid:
On both Pt(111) and Pt(100) HNO₃ is progressively deoxygenated to HNO₂ and "NOH via 2 and 3 electron transfer steps, respectively.

The formed HNO₂ disproportionates in acid and yields "NO on both surfaces, leading to rapid blocking on Pt(111).

"NO is a key intermediate of nitrate reduction in acid. For the complete reduction of nitrate to ammonium under potential-static conditions, "NO reduction to NH₂ must be feasible at the same potentials where nitrate reduction to "NO occurs, otherwise the latter acts as a poison.

The mechanistic structure-sensitivity of "NO reduction renders the mechanism of HNO₂ reduction also structure-sensitive: on Pt(111), "NO is reduced to "NOH at sufficiently low potentials (below +0.4 V for "NO on-top and below +0.25 V for "NO on fcc-hollow sites). On Pt(100), low-coverage "NO is reduced to "NOH already at more positive potentials (i.e. below ca. +0.6 V), but high-coverage "NO requires more negative potentials.

The formed "NOH will be reduced to NH₂ if the potential allows, or will dimerize to H₂N₂O₂ on both surfaces.

The "NOH formed on Pt(100) will be either reduced to NH₂ or oxidized back to "NO, depending on the applied potential.

Overall, our study illustrates the complexity of the potential-controlled transformations of nitrogen-containing species on electrified catalytic surfaces. In multi-electron reactions such as nitrate reduction, the complexity stems from the many oxidation states of nitrogen from HNO₂ (+5) to NH₂ (−3). In addition, more than one adsorbate or stable product can form at a given oxidation state of +1 which allows for mechanistic structural sensitivity. This interpretation is general for the nitrogen cycle: nitrate here acts merely as the source of nitrogen-containing adsorbates, which then undergo redox processes depending on the electrode potential and the platinum facet with which it interacts.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.electacta.2018.03.126.

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