

Direct Reduction of Nitrite to N<sub>2</sub> on a Pt(100) Electrode in Alkaline Media

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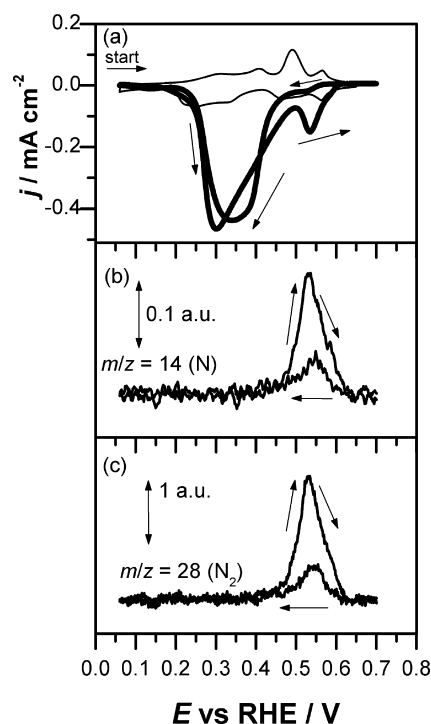
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**Abstract:** The selective reduction of NO<sub>2</sub><sup>−</sup> to N<sub>2</sub> in 0.1 M NaOH was obtained at a Pt(100) electrode in a narrow but distinct potential region. This is the first report of such selectivity for this reaction on Pt(100), which is known to be the most catalytically active platinum surface toward NO<sub>2</sub><sup>−</sup> reduction in alkaline media. Both ammonia and nitrous oxide are ruled out as possible reaction intermediates on the basis of online electrochemical mass spectrometry. Based on earlier work on ammonia oxidation, NH<sub>2</sub> adsorbates are speculated to be involved in the reaction mechanism.

Wastewater remediation by means of electrochemical techniques has become an active field of research.<sup>1</sup> A specific challenge in this area is the abatement of nitrite NO<sub>2</sub><sup>−</sup> and nitrate NO<sub>3</sub><sup>−</sup> via electrochemical reduction, provided that selectivity to harmless N<sub>2</sub> is achieved. This task is by no means trivial, as nature performs this multielectron conversion with a multienzyme array.<sup>2–5</sup> Here we report the remarkable direct reduction of nitrite to N<sub>2</sub> on a monometallic and monocrystalline Pt surface in alkaline media. N<sub>2</sub> production from NO<sub>2</sub><sup>−</sup>/NO<sub>3</sub><sup>−</sup> has been claimed before, although only with multimetallic systems, such as Pd/Sn/Au,<sup>6,7</sup> Cu/Pd,<sup>8</sup> or Rh on Ti<sup>9</sup> for NO<sub>3</sub><sup>−</sup> reduction and Sn-modified Pd, Rh, Ru, Ir electrodes for HNO<sub>2</sub> reduction.<sup>10</sup> However, we note that only for the Cu/Pd catalyst the N<sub>2</sub> formation was observed *in situ* during voltammetry using online mass spectrometry (see below).

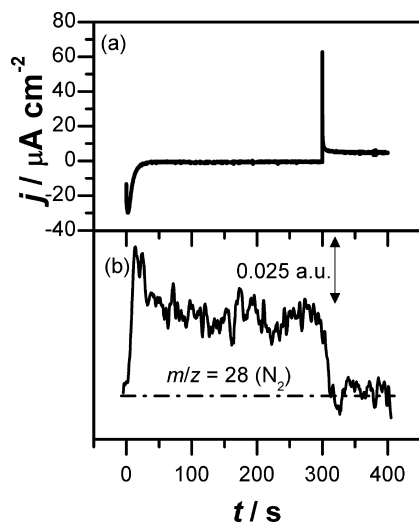
Among the transition metals, Pt exhibits a special activity toward the reduction of various nitrogen-containing molecules.<sup>3,11</sup> Different well-ordered monocrystalline Pt surfaces can display dramatically different behavior toward a certain reaction, as evidenced for NH<sub>3</sub> oxidation.<sup>3,12,13</sup> Structure sensitivity for nitrite reduction at Pt electrodes has been demonstrated in alkaline media,<sup>3,14,15</sup> while in acidic media HNO<sub>2</sub> reduction is largely insensitive to the surface structure.<sup>3,16</sup> In agreement with earlier results of the Kita group,<sup>14</sup> we find that the reactivity of the three Pt basal planes in a nitrite-containing 0.1 M NaOH solution increases in the order Pt(111) < Pt(110) < Pt(100) (see Figure S1). The Pt(100) shows a large reduction peak centered at 0.35 V vs RHE, which was also previously reported<sup>14</sup> and ascribed to NH<sub>3</sub> formation, as evidenced by prolonged constant-potential electrolysis. Ye et al.<sup>14</sup> also showed that Pt(100) can subsequently reoxidize NH<sub>3</sub> to N<sub>2</sub> in the same scan at ca. 0.6 V. Indeed, Pt(100) has a unique activity for the oxidation of NH<sub>3</sub> to N<sub>2</sub>.<sup>12,13,17</sup> However, the strong influence of the pretreatment on the electrochemistry of the Pt(100) surface in alkaline media<sup>18</sup> has prompted us to reinvestigate NO<sub>2</sub><sup>−</sup> reduction in 0.1 M NaOH at a Pt(100) electrode. Surprisingly, we observed the highly selective direct reduction of NO<sub>2</sub><sup>−</sup> to N<sub>2</sub> on Pt(100), to be reported on below. This is a significant finding as such an observation has not been made before for a (monometallic) electrocatalyst.

Figure 1a, shows the first voltammetric scan of a Pt(100) electrode, in a 0.1 M NaOH + 2 mM NaNO<sub>2</sub> solution, starting



**Figure 1.** Cyclic voltammetry during OLEMS measurements (a) and ion current profiles for  $m/z = 14$  (b) and  $m/z = 28$  (c) in 0.1 M NaOH containing 2 mM NaNO<sub>2</sub>. The working electrode was a Pt(100) electrode,  $\nu = 1$  mV/s. The arrows indicate the direction of the potential sweep. The blank voltammogram inserted in panel (a), thin line, was recorded at  $\nu = 50$  mV/s.

from 0.06 V sweeping in the positive direction (see Supporting Information for additional details). The voltammetric profile features two reduction peaks, one between 0.25 and 0.45 V and a second smaller centered around 0.55 V, respectively. This latter feature was not reported in the experiments of the Kita group.<sup>14</sup> It is reasonable to assume that this discrepancy stems from an improvement in the quality of the Pt(100) surface. The blank voltammogram of our electrode is also included in Figure 1: it can be compared to the CV profiles reported in a recent study from our group.<sup>18</sup> In brief, the peaks at 0.48 V (positive-going) and 0.28 V (negative-going) evidence the presence of long-range (100) terraces, along with a minor amount of shorter (100) domains and (110) defects. Cycling a Pt(100) electrode in alkaline media has been shown to compromise long-range (100) order and to introduce defects;<sup>18</sup> consequently, we stress that only freshly flame annealed electrodes were used in the present study. Moving to the other panels of Figure 1, real-time monitoring of the conceivable gaseous products (N<sub>2</sub>, NO, N<sub>2</sub>O) during the voltammetric scan using online mass spectrometry (OLEMS)<sup>19</sup> shows the formation of N<sub>2</sub> in the restricted potential range of the second voltammetric peak around 0.55 V



**Figure 2.** Chronoamperometric profile during OLEMS measurements (A) and ion current profiles for  $m/z = 28$  (B) in 0.1 M NaOH containing 2 mM  $\text{NaNO}_2$ . The working electrode was a Pt(100) electrode,  $\nu = 1$  mV/s. The electrode was kept at 0.55 V for 300 s, followed by a potential step to 0.65 V. The  $m/z$  current immediately before  $t = 0$  is also shown.

(see Figure 1b and c). Significantly, NO and  $\text{N}_2\text{O}$  were not detected during the nitrite reduction voltammetry.

The reduction peak associated with the detection of  $\text{N}_2$  (and its fragment N) appears both in the positive-going and in the negative-going scan, although it is much smaller in the latter case. This positively parallels the lower MS current detected for  $\text{N}_2$  in the negative-going scan. Especially the reduction in the positive-going scan is strong evidence in favor of a direct and selective reduction of  $\text{NO}_2^-$  to  $\text{N}_2$ , as opposed to  $\text{N}_2$  formation via intermediate  $\text{NH}_3$  oxidation, as the latter reaction would have led to an oxidation current. Ammonia is a ubiquitous product of the reduction of nitrogen species at Pt electrodes and was reported by Ye et al. to be the main—even only—product in the broad reduction peak between 0.25 and 0.45 V,<sup>14,15</sup> a conclusion that we have confirmed with an experiment described in the Supporting Information (Figure S2). To exclude the simultaneous formation of  $\text{NH}_3$  during the  $\text{N}_2$  formation peak at 0.55 V (a potential at which Pt(100) is capable of oxidizing ammonia<sup>13</sup>), we designed an experiment to rule out the occurrence of  $\text{NH}_3$  as an intermediate or a byproduct.

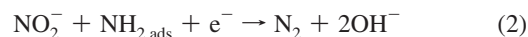
After pretreating the electrode as described above, the Pt(100) was immersed at  $E = 0.06$  V and the potential was stepped directly to a  $\text{N}_2$  generating potential of  $E = 0.55$  V, kept at this value for 300 s, and next stepped to  $E = 0.65$  V. In this way, if any ammonia would be formed at  $E = 0.55$  V, we would expect some of it to escape into solution, and it should then be oxidized at  $E = 0.65$  V as the Pt(100) electrode should oxidize  $\text{NH}_3$  to  $\text{N}_2$  at that potential, but not reduce nitrite to  $\text{N}_2$ . Figure 2 shows the results of this experiment. During the first 300 s at 0.55 V, a small reduction current is recorded due to nitrite reduction (Figure 2a), along with clear evidence of continuous  $\text{N}_2$  evolution as recorded in the OLEMS (Figure 2b). However, after the potential has been stepped to 0.65 V,  $\text{N}_2$  evolution immediately reduces to the background level, showing that no appreciable  $\text{NH}_3$ , oxidizable at 0.65 V, was generated during nitrite reduction at 0.55 V. Therefore, these results offer additional evidence for the selective and direct reduction of  $\text{NO}_2^-$  to  $\text{N}_2$  at Pt(100). The same experiment, but with the first potential step to 0.35 V, yields significant  $\text{N}_2$  detection at  $E = 0.65$  V during the second step, showing the formation of ammonia at 0.35 V (Figure S2).

The direct involvement of  $\text{NH}_3$  was also ruled out by an additional experiment shown in the Supporting Information (Figure S3). A Pt(100) electrode was immersed in a nitrite-containing 0.1 M NaOH solution, and a voltammetric profile was recorded in the so-called hanging meniscus rotating disk configuration (HMRD)<sup>20</sup> (to enhance transport to the electrode). Subsequently, increasing amounts of  $\text{NH}_3$  were added: a detrimental effect on the peak related to  $\text{N}_2$  formation was observed. In addition, the reduction peak at 0.35 V is retarded to higher potentials. Therefore,  $\text{NH}_3$  cannot be a key participant in the formation of  $\text{N}_2$  and, moreover, its presence could even suppress  $\text{N}_2$  formation and influence its own formation in the first peak. The HMRD setup also allows modulation of the rotation rate. Figure S4 shows that a change in rotation rate does not affect the magnitude of the peak current of the feature related with  $\text{N}_2$  production. This piece of evidence indicates that the reaction is not under diffusion control, possibly involving only surface-bound species. Moreover, if  $\text{NH}_3$  were an intermediate in the  $\text{N}_2$  formation, an increase of the rotation rate would cause a decrease in the peak current by enhancing the escape of  $\text{NH}_3$  away from the electrode. However, this effect is not observed (Figure S4).

The elucidation of the mechanistic steps leading to  $\text{N}_2$  formation and the identification of the surface intermediates involved in this reaction remain somewhat elusive, especially since no additional information concerning the reaction intermediates can be inferred from e.g. FTIR (Fourier-Transform Infrared) spectroscopy in the external reflection configuration, due to the accumulation of gas bubbles in the thin layer, disturbing the reflectance measurements. However, on the basis of previous works concerning ammonia oxidation and its adsorbates in the  $E = 0.4$ – $0.55$  V range in alkaline media,<sup>12–14,17,21,22</sup>  $\text{NH}_{2,\text{ads}}$  was suggested as a stable surface-adsorbed intermediate up to ca. 0.5 V. The potential for which we report  $\text{N}_2$  evolution corresponds to the foot of the main wave of  $\text{NH}_3$  oxidation on Pt(100). For this surface, it has been suggested that two  $\text{NH}_2$  combine to form hydrazine to finally oxidize to  $\text{N}_2$ , this reaction made possible by the high  $\text{NH}_{2,\text{ads}}$  coverage.<sup>13,23</sup> On the other hand, the OLEMS and voltammetric data for nitrite reduction described above show only reduction currents, and no evidence for the ammonia oxidation, or the direct involvement of ammonia in the  $\text{N}_2$  formation reaction, was obtained. We therefore propose the following tentative reaction scheme. First  $\text{NO}_2^-$  is reduced to  $\text{NO}_{\text{ads}}$ , followed by N–O bond breaking leading to an  $\text{NH}_x$  intermediate, presumably  $\text{NH}_{2,\text{ads}}$ :



Next, the  $\text{NH}_{2,\text{ads}}$  intermediate must yield  $\text{N}_2$  in a reduction reaction:



with  $\text{NO}_2^-$  in the solution phase, or involving  $\text{NO}_{\text{ads}}$  in an intermediate step. Various pieces of evidence discussed in this communication, in fact, suggest that a slow, surface-confined reaction should be operative in the  $\text{N}_2$  formation region. Further investigations are currently underway in our laboratory to obtain additional insight into the intermediate species.

In conclusion, we have reported here a unique direct and selective reduction of  $\text{NO}_2^-$  to  $\text{N}_2$  at a Pt(100) electrode in 0.1 M NaOH at a potential close to 0.55 V. The combination of voltammetry and OLEMS exclude  $\text{N}_2\text{O}$  and ammonia as possible reaction intermediates. In light of previous work on  $\text{NH}_3$  oxidation in the same electrolyte, we propose that  $\text{NH}_{2,\text{ads}}$  plays a key mechanistic role, reacting with  $\text{NO}_2^-$  or  $\text{NO}_{\text{ads}}$  to form  $\text{N}_2$  in a reduction reaction.

Our work not only represents a unique example of  $\text{NO}_2^-$  removal with the production of a benign species but also provides a clear illustration of a highly specific reduction reaction operative on Pt(100), a surface which is usually better known as a very selective oxidation catalyst.<sup>12,13,21,24</sup> Our results could potentially be extended to Pt nanoparticulate systems featuring (100) preferential orientation<sup>24,25</sup> and thereby to the design of new electrocatalysts for nitrite and nitrate abatement.

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**Supporting Information Available:** Experimental details, a comparison of the behavior of the three basal planes toward nitrite reduction, an OLEMS measurement evidencing  $\text{NH}_3$  formation in the major peak, and experiments probing the effect of  $\text{NH}_3$  addition and the influence of rotation rate in HMRDE configuration. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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