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The study of NO adsorbate layers on platinized platinum in the liquid phase with cyclic voltammetry, DEMS and FTIRS

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Abstract. The irreversible adsorbates formed after exposure of platinum to an NO-containing solution were studied with Differential Electrochemical Mass Spectrometry (DEMS), Fourier-Transform Infrared Spectroscopy (FTIRS) and cyclic voltammetry. DEMS and FTIRS show that only a very small amount of N_2O is formed in the reduction of the adsorbate, indicating that mainly non-volatile products are formed. FTIRS shows, in addition, vibrations of NO at wavenumbers characteristic of adsorbed NO on Pt(100) and Pt(110) sites. These two different adsorption sites are characterized by separate reduction peaks in the cyclic voltammogram. Further, it was established with FTIRS that the adsorbate is transformed to N_2O and NH_4^+ in the reduction, and to NO_3^- in the oxidation. Analysis of the charges involved in the reduction and oxidation of the irreversible adsorbates demonstrates that coadsorbates are present next to NO. The coadsorbates consist of adsorbed nitrogen atoms, formed by the dissociation of NO. This view is supported by previously reported studies in Ultra High Vacuum (UHV). A new mechanism for the reduction of NO to N_2O in the liquid phase is proposed on the basis of NO dissociation.

Introduction

The reduction of nitric oxide in acid medium on platinum electrodes has been extensively studied using electrochemical techniques^{1–12}. The selectivity of the reaction was found to depend largely on the reduction potential. At potentials above 0.35 V, N_2O is found as the only product^{1–4}. Several mechanisms have been proposed to account for N_2O formation. The most frequently reported mechanism^{1,3–6,8–10} consists of a single electron reduction of the NO molecule, followed by dimerization and N_2O formation according to;

Some authors have proposed HNO_{ads} instead of NOH_{ads} as an intermediate in the formation of N_2O ^{1,3,4,10}. So far, no direct evidence has been presented for the existence of NOH or HNO as an intermediate in the NO reduction. A second mechanism, based on a study in concentrated perchloric acid⁷, consists of the disproportionation of NO followed by N_2O formation and electron transfer according to:

Rotating disk experiments on smooth platinum electrodes demonstrated that the NO reduction to N_2O is diffusion limited^{9–11}.

At potentials lower than 0.35 V, NH_2OH and NH_4^+ are observed in addition to N_2O ^{1–4,12}. The product distribution depends on the reduction potential and the supporting electrolyte. Maximum selectivities for hydroxylamine of 70%¹ and 78%² were found in concentrated sulfuric acid. Strongly adsorbing species like chloride, carbon monoxide³, and sulfur¹² have a promoting effect on the hydroxylamine selec-

tivity. It is generally proposed that the NOH_{ads}/HNO_{ads} species is the intermediate in the formation of hydroxylamine according to:

Ammonium can be formed by a hydrogenolysis of NH_2OH ^{1,3,5,7} or $NHOH$ ³ according to:

It has recently been demonstrated that a close correlation exists between the properties of adsorbed NO molecules in the liquid phase and in Ultra High Vacuum (UHV). IR studies on platinum single crystal electrodes show that solvent coadsorption has a limited effect (35–70 cm^{-1}) on the vibration frequencies with respect to UHV data^{14–17}. The adsorption of NO is structure sensitive in UHV as well as in the liquid phase and the N–O stretch vibration was found to vary by 125 cm^{-1} for the three basal planes of platinum. This implies that UHV studies are highly relevant to adsorption processes in the liquid phase. Particularly interesting is the observation in UHV that partial dissociation of NO occurs at room temperature on Pt(100)¹⁸, Pt(310)¹⁸ and Pt(410)^{18–20} in contrast with Pt(111)²¹, Pt(110)^{22,23}, Pt(210)²⁴ and polycrystalline platinum²⁵ for which only molecular adsorption was found. Palladium behaves qualitatively in the same way as platinum; of the three basal planes, Pd(100) displays partial dissociation at room temperature, while molecular adsorption was observed on Pd(110)²⁶ and Pd(111)^{26,27}.

This paper describes the application of cyclic voltammetry, Differential Electrochemical Mass Spectrometry (DEMS) and Fourier-Transform IR spectroscopy (FTIRS) to the characterization of the adsorbates formed after contact between platinized platinum and NO-containing solutions. These results will be interpreted in the context of single-crystal data ob-

tained in UHV studies. A new mechanism for N_2O formation in the liquid phase will be proposed that is based on NO dissociation, in contrast with the generally held view that NOH/HNO adspecies are the key intermediates in N_2O formation.

Experimental

Infrared measurements were performed with a Biorad FTS 45A spectrometer, equipped with a liquid-nitrogen cooled MCT detector. All spectra were recorded with 4 cm^{-1} resolution. The electrochemical cell, made of glass, equipped with a CaF_2 prism with 65° beveled edges to obtain a high reflection angle was placed on top of the sample room. The electrode consisted of a platinum disk of 9 mm diameter embedded in teflon (PTFE). The infrared beam was focused on the electrode by one flat and one ellipsoidal mirror, with which the optimal spot size could be obtained. A polarizer was placed in the sample room of the spectrometer to obtain *p*-polarized light.

DEMS measurements were performed with a Leybold Quadruvac PGA 100 mass spectrometer. The experimental setup is similar to the one described previously¹³. The products were examined for N_2O ($m/z = 44$), N_2 ($m/z = 28$) and NH_3 ($m/z = 17$).

Electrochemical measurements were performed with an Autolab PG-STAT 20 computer-controlled potentiostat. The rotating-ring-disk measurements were performed with a Tacussel BI-PAD bipotentiostat. A Hg/Hg₂SO₄ electrode was used as a reference electrode. All potentials will be referred to the reversible hydrogen electrode (RHE). All measurements were performed with platinized platinum, prepared by electrodeposition from a H_2PtCl_6 solution. The electrodes used in the DEMS and IR measurements are characterized by a real area of 124 cm^2 and 10 cm^2 , respectively, as derived from the charge involved in the hydrogen desorption in the voltammogram in $0.5\text{ M H}_2\text{SO}_4$. Potential cycling between 0 and 1.5 V was carried out until a stable voltammogram was obtained. Electrolytes were prepared using ultrapure water ($18.2\text{ M}\Omega$) obtained with an Elga water purification system. In the infrared experiments $0.1\text{ M H}_2\text{SO}_4$ (Merck p.a.) was used and, for cyclic voltammetry and the DEMS measurements, $0.5\text{ M H}_2\text{SO}_4$ was used. Oxygen was removed from the electrolyte with Argon (Hoek Loos, purity 4.6). Before use, NO (Hoek Loos, purity 2.0) was bubbled through a concentrated KOH solution to remove impurities.

Results

A platinum electrode was exposed to NO-saturated $0.5\text{ M H}_2\text{SO}_4$ electrolyte for 10 minutes. During this adsorption process the open circuit potential rose to 0.93 V and then declined to 0.90 V. With DEMS, no gaseous products such as N_2 or N_2O were found within the detection limit of the apparatus during adsorption at open circuit potential. After replacement of the electrolyte with fresh $0.5\text{ M H}_2\text{SO}_4$, a scan was started at 0.90 V in the cathodic direction, depicted as the solid line in Figure 1. The cyclic voltammogram shows that the electroreduction of the adsorbate starts at 0.43 V, prior to the formation of adsorbed hydrogen which begins at 0.38 V in NO-free electrolyte. The main part of the reduction takes place in the hydrogen region, consisting of two equally sized peaks at 0.28 V and 0.22 V. The total charge involved in the reduction is $398\text{ }\mu\text{C}/\text{cm}^2$. The electrode area was determined from the anodic charge in the hydrogen region in blank electrolyte. DEMS demonstrates that N_2O is formed in the potential region between 0.68 and 0.28 V with a maximum at 0.40 V. No N_2 was observed in this potential region. Furthermore, the cyclic voltammogram contains a small reduction peak at 0.78 V and Figure 1 shows that this reduction is not correlated with N_2O formation, but is probably due to the reduction of platinum oxides. The amount of N_2O was determined by comparison with the amount of CO_2 detected after oxidation of a monolayer of CO. When the different relative ionization probabilities of both molecules and the fragmentation patterns are taken into account, it follows that the amount of N_2O that is formed in the double layer region equals less than 1% of a monolayer. A small reduction current was observed in the double layer region when an experiment was

Figure 1. DEMS measurement obtained after adsorption of an NO-containing electrolyte at open-circuit potential. First (—) and second (---) cycle. Scan rate 2 mV/s , $m/z = 44$ (N_2O^+). Electrolyte $0.5\text{ M H}_2\text{SO}_4$, real area 124 cm^2 .

carried out with increased sensitivity. This reduction current is too small to observe in Figure 1. Thus, it follows that the formation of N_2O is accompanied by charge transfer. Note that such a small amount of N_2O could only be observed due to the roughness of the electrode. It is remarkable that the formation of N_2O decreases at a potential, where reduction of the adsorbate starts in earnest in the cyclic voltammogram. Since the cell design causes a tailing of the product mass peak, it is difficult to establish exactly at which potential the formation of N_2O stops. However, it is clear from Figure 1 that no N_2O is formed at potentials below 0.28 V. Since only small amounts of N_2O are observed it can be concluded that the majority of the electroreduction products are non-volatile. Indeed, the possible products hydroxylamine and ammonium^{1-4,12} are protonated under these reaction conditions. Our observations are in agreement with literature data which show that, in the continuous reduction of NO on platinum, N_2O is observed as the only product at potentials above 0.35 V while at lower potentials NH_2OH and NH_4^+ are also observed¹⁻⁴.

Single-crystal studies have shown that the electroreduction of adsorbed NO is structure-sensitive¹⁴⁻¹⁷. For Pt(100) and Pt(110) a peak potential was reported at 0.19 V and 0.27 V, respectively. These potentials are close to the values found in our measurements which seems to suggest that NO is present on (100) and (110) related sites on our electrode. For Pt(111) two peaks are reported at 0.12 V and 0.3 V, the latter coinciding with the peak observed on Pt(110). No significant contribution is observed in our measurements in the potential region characteristic for NO reduction on Pt(111) sites. We will return to this point later.

In a second experiment NO was adsorbed at 0.68 V. A steady state reduction current is now observed together with a constant N_2O mass signal ($m/z = 44$). Both the reduction current and the N_2O mass signal increase upon convection of the solution, indicating that the reaction is diffusion limited. It is obvious that the reduction current and the N_2O formation are correlated. However, no quantitative correlation can be established because the fraction of product molecules that reaches the vacuum chamber is lowered upon convection of the solution. The amount of N_2O and the reduction charge ob-

Figure 2. Infrared spectra ($\Delta R/R_0$, $\Delta R = R_0 - R_1$) obtained after adsorption for 10 minutes at 0.68 V. First spectrum recorded at 0.78 V (R_0), second spectrum at 0.48 V (R_1). Electrolyte 0.1M H_2SO_4 . Resolution 4 cm^{-1} .

served after electrolyte replacement in the cathodic scan are equal to those observed after adsorption at open-circuit potential.

The IR spectrum in Figure 2 was obtained after 10 minutes adsorption at 0.68 V in NO saturated electrolyte. The infrared spectrum, given as $\Delta R/R_0$ ($\Delta R = R_0 - R_1$), was obtained by changing the electrode potential from 0.78 (R_0) to 0.48 V (R_1), recording a single beam spectrum at every potential. The single-beam spectrum obtained at 0.78 V was taken as the reference. The spectrum in Figure 2 contains a positive band at 2231 cm^{-1} , that can be assigned to the N-N stretch vibration of dissolved N_2O in the thin layer²⁸. The small band at 1285 cm^{-1} belongs to the N-O stretch vibration of N_2O ²⁸. The formation of N_2O was only observed in the first cathodic scan between 0.78 and 0.48 V. A repeated potential excursion from 0.78 to 0.48 V did not result in the additional formation of N_2O . The integrated N_2O absorbance is roughly 50 times lower than the integrated CO_2 absorbance found after oxidation of a monolayer of CO, confirming the above observation with DEMS that the amount of N_2O formed is very small. Given this fact, it is difficult to establish from the IR spectrum whether or not NO has disappeared in the formation of N_2O . The formation of N_2O has also been observed with IR spectroscopy on single crystal electrodes. Surprisingly, N_2O was only observed for Pt(100), and not for the Pt(110) and Pt(111) crystal planes¹⁴.

In addition to the vibrations of N_2O , bipolar peaks are observed at 1790/1730 cm^{-1} and 1650/1590 cm^{-1} . The bipolar character of these peaks arises from a shift to lower wavenumbers as the electrode potential is decreased. This phenomenon, the so-called Stark effect, is well known for adsorbed CO on platinum and it was also recently observed for adsorbed NO¹⁴⁻¹⁷. Moreover, the Stark effect proves that the IR features are connected to adsorbed species. An infrared study of NO adsorbed on single crystal electrodes produced a bipolar peak centred at 1640 cm^{-1} for Pt(100) after a potential shift from 0.65 to 0.95 V. The same frequency was also found on this crystal plane for a (4×2) adsorbate layer with an NO coverage of 0.5 in UHV²⁹. A bipolar peak centred at 1700 cm^{-1} was found for Pt(111), but for Pt(110) no bipolar band was found after shifting the potential from 0.65 to 0.95¹⁴. However, a band at 1760 cm^{-1} was observed after stripping the adsorbate in a potential step from 0.8 to 0.1 V¹⁴. In UHV experiments, a vibration at 1760 cm^{-1} was found on Pt(110)²², that was assigned to linearly bonded NO. On the basis of these single crystal data, the bipolar vibration at 1790/1730 cm^{-1} can be ascribed to NO adsorbed on (110) sites and the bipolar band at 1650/1590 cm^{-1} can be as-

cribed to NO adsorbed on (100) sites. Furthermore, it was found in UHV studies that different IR vibrations exist for adsorbed NO at low and high coverages. The NO vibrations found in our experiments demonstrate that we are dealing with high NO coverages.

At low adsorbate coverages, the bipolar peak at 1650/1590 cm^{-1} remains present in the spectrum, but the bipolar band at 1790/1730 cm^{-1} was no longer observed. The lowest adsorbate coverage studied with IR was 130 $\mu C/cm^2$, roughly 30% of the maximum charge found in reduction.

Lowering the potential from 0.48 to 0.08 V does not yield peaks related to the additional formation of N_2O , but a broad positive band occurs at 1460 cm^{-1} , as shown in Figure 3a. A negative band is present at 1210 cm^{-1} , that can be assigned to a decrease of HSO_4^- concentration due to migration. After performing reference experiments with $(NH_4)_2SO_4$, the band at 1460 cm^{-1} could be ascribed to NH_4^+ ions in the thin layer, in accordance with a previous report³⁰. No vibrations were observed that could be assigned to NH_2OH formation. Figure 3 shows that increasing the potential from 0.68 to 1.38 V after adsorption generates a double peak in the IR spectrum at 1356 and 1393 cm^{-1} . Exactly the same vibrations were found in reference experiments where nitrate ions were allowed to diffuse into the thin layer. Reference experiments with nitrite produced a vibration at 1239 cm^{-1} . No vibration was observed at this wavenumber in our experiments, indicating that complete oxidation of the adsorbate to nitrate has occurred. The positive band at 1210 cm^{-1} stems from an increase in HSO_4^- concentration due to migration.

A rotating ring-disk experiment was performed to obtain additional information on the products formed during the reduction of the adsorbate. The adsorption was carried out at 0.48 V in NO-saturated electrolyte for 10 minutes followed by

Figure 3. Infrared spectra ($\Delta R/R_0$, $\Delta R = R_0 - R_1$) for the reduction (top spectrum) and the oxidation (bottom spectrum) obtained after 10 minutes adsorption at 0.68 V. For the reduction and oxidation $E_1 = 0.68$ V and $E_2 = 0.68$ V, after potential excursions to 0.03 V and 1.38 V, respectively. Electrolyte 0.1M H_2SO_4 . Resolution 4 cm^{-1} .

Table I The charge involved in reduction $\bar{Q}_{\text{red}}$ of the adsorbate layer as a function of cathodic adsorption current density i_{ads} . Adsorption was carried out at 0.48 V for 10 minutes.

i_{ads} ($\mu\text{A}/\text{cm}^2$)	$\bar{Q}_{\text{red}}$ ($\mu\text{C}/\text{cm}^2$)
0.44	206
0.76	210
6.6	353
13.2	409

Table II The ratio $\bar{Q}_{\text{ox}}/\bar{Q}_{\text{red}}$ as a function of the reduction charge $\bar{Q}_{\text{red}}$. Adsorption was carried out at 0.48 V for 10 minutes.

$\bar{Q}_{\text{red}}$ ($\mu\text{C}/\text{cm}^2$)	$\bar{Q}_{\text{ox}}/\bar{Q}_{\text{red}}$
206	1.06
210	0.90
353	0.73
409	0.75

electrolyte replacement; a constant adsorption current was observed. It is possible with this experiment to discriminate between the formation of ammonium and hydroxylamine, since only the latter is sensitive to oxidation on the platinum ring. The chemisorbed species are reduced after adsorption in a cathodic scan, while the ring was kept at a constant potential of 1.18 V at a rotation speed of four revolutions per second. No oxidation current was observed on the ring electrode during reduction of the adsorbate, demonstrating that ammonium ion is the only product formed.

Information on the composition of the adsorbate can be obtained by analysing the charges involved in reduction and oxidation of the adsorbate layer. First, the reduction charge $\bar{Q}_{\text{red}}$ is determined by performing two cycles in the hydrogen region. The second cycle equals the voltammogram of the blank electrolyte and the charge $\bar{Q}_{\text{red}}$ is determined by subtracting the second from the first cycle. Then, the adsorption procedure is repeated, but now the adsorbate is oxidized. Five cycles in the oxide region are necessary for complete removal of the adsorbate layer. The concurrent charge $\bar{Q}_{\text{ox}}$ is determined by using the fifth cycle as the reference. The ratio $\bar{Q}_{\text{ox}}/\bar{Q}_{\text{red}}$ gives information on the adsorbate composition. The NO concentration in the solution was found to have an effect on the adsorbate coverage as well as the adsorbate composition. It has been shown that the NO reduction to N_2O is diffusion-limited in this potential region⁹⁻¹¹, so that the adsorption current can be taken as a measure for NO concentration. The charge that is necessary for reduction of the adsorbate can be taken as an estimate for the coverage. Table I shows the relation of the charge $\bar{Q}_{\text{red}}$ involved in the adsorbate reduction with the NO concentration as indicated by the adsorption current i_{ads} . The ratio $\bar{Q}_{\text{ox}}/\bar{Q}_{\text{red}}$ gives information on the adsorbate composition and again $\bar{Q}_{\text{red}}$ can be taken as an estimate of the adsorbate coverage. Table II presents the ratio $\bar{Q}_{\text{ox}}/\bar{Q}_{\text{red}}$ as a function of $\bar{Q}_{\text{red}}$. It follows from the data that adsorbate composition changes with coverage. These results will be discussed in the next section.

Discussion

The IR measurements clearly demonstrate that adsorbed NO is present after the platinum electrode has been in contact with an NO-containing solution. To our knowledge, it is the first time that adsorbed NO has been observed on polycrystalline platinum in the liquid phase with IR spectroscopy. The assignment of the various NO vibrations is based on single-crystal studies. Our results confirm once more that the vibrational characteristics of NO adsorbed on platinum in the liquid phase are very similar to those for UHV conditions.

From our cyclic voltammetry and IR spectroscopy data, we conclude that NO is present on (100) and (110) related sites, while no features characteristic for adsorption on (111) sites were found. Close comparison of the hydrogen peaks in the voltammogram in 0.5M H_2SO_4 with single crystal data³¹ suggests that the hydrogen peak at 0.10 V can be assigned to (110) sites, while the peak at 0.24 V coincides with the peak potential for Pt(310) sites. The latter consists of (100) terraces divided by steps in a (110) geometry. No voltammetric features are present that can be assigned to Pt(111) and this is consistent with the absence of the NO vibration for Pt(111) sites in IR spectroscopy.

The reduction of NO adsorbates to NH_4^+ may be considered as a hydrogenation reaction of NO involving adsorbed hydrogen, although some opposing facts arise from the experimental work. Cyclic voltammetry has shown that the reduction of NO proceeds more easily on Pt(110) than on Pt(100)¹⁶, as indicated by the higher reduction potential. This is opposite to the trend observed for adsorbed hydrogen, which is formed at a higher potential on Pt(100) with respect to Pt(110)³¹. On Pt(110) NO is reduced at a potential at which no adsorbed hydrogen is present and this seems to suggest that adsorbed hydrogen is not in a simple manner involved as a reactant in the reduction of NO. This situation is similar to the oxidation of CO to CO_2 on platinum which occurs at potentials prior to oxide formation. The data suggest that the structure sensitivity of the reaction is not connected to the Pt-H interaction but to the Pt-NO interaction. The different NO stretch vibrations observed on Pt(110) and Pt(100) indicate that the metal-adsorbate interaction is clearly structure sensitive.

Our conclusion that high NO coverages are present in the potential region between 0.68 and 0.38 V is in contradiction with electrochemical literature that supports the theory that NO is reduced to NOH_{ads} or HNO_{ads} at these potentials, leading to the formation of $\text{N}_2\text{O}^{1-12}$. However, our IR data do not prove unambiguously that NO_{ads} is the only adsorbate present on the surface. It is possible that the vibrations of NOH_{ads} or HNO_{ads} are too weak to observe in our experiments.

Additional information on the adsorbate composition can be obtained from analysing the $\bar{Q}_{\text{ox}}/\bar{Q}_{\text{red}}$ ratios given in Table II. The quantities $\bar{Q}_{\text{ox}}$ and $\bar{Q}_{\text{red}}$ can be written as:

$$\bar{Q}_{\text{ox}} = Q_{\text{H}}^0 \theta_{\text{tot}} n_{\text{ox}}$$

$$\bar{Q}_{\text{red}} = Q_{\text{H}}^0 \theta_{\text{tot}} n_{\text{red}}$$

with Q_{H}^0 the anodic charge of the hydrogen region, θ_{tot} the total adsorbate coverage and n_{ox} and n_{red} are the average number of electrons involved in the oxidation or reduction of a single adsorbate species, respectively. From these equations it follows that the ratio $\bar{Q}_{\text{ox}}/\bar{Q}_{\text{red}}$ is equal to $n_{\text{ox}}/n_{\text{red}}$. In combination with the rotating ring-disk experiment, our IR experiments have shown that NH_4^+ is the only product in the adsorbate reduction, and NO_3^- is the only product in the oxidation. When NO is the only adsorbate present on the surface, the ratio $\bar{Q}_{\text{ox}}/\bar{Q}_{\text{red}}$ is 3/5, as follows from the corresponding reduction and oxidation reactions of NO:

However, Table II clearly shows that significantly higher $\bar{Q}_{\text{ox}}/\bar{Q}_{\text{red}}$ ratios are found, indicating that coadsorbates exist with a higher $n_{\text{ox}}/n_{\text{red}}$ ratio. These coadsorbates are apparently reduced and oxidized in the same potential region as adsorbed NO, since no separate peaks were observed with cyclic voltammetry. NOH_{ads} and HNO_{ads} are characterized by an $n_{\text{ox}}/n_{\text{red}}$ ratio of 1, according to the following reduction and oxidation reactions:

In UHV partial dissociation of adsorbed NO on the Pt(410), Pt(310) and the Pt(100) plane have been observed at room temperature. The presence of Pt(100) sites on our electrode surface has been demonstrated by the characteristic NO vibration and by the peak potentials for NO reduction in the cyclic voltammogram of Figure 1. In addition, the peak potential of 0.24 V for the strongly bonded hydrogen adspecies corresponds with the peak potential for stepped (100) surfaces³¹ and therefore supports the view that 100 related sites are present on the electrode surface. On the basis of these facts we feel that the possibility of NO dissociation must be considered, resulting in the formation of adsorbed nitrogen and oxygen atoms. The oxygen atoms can either be reduced to water or reside on the surface, depending on the adsorption conditions. Adsorbed nitrogen atoms are characterized by an $n_{\text{ox}}/n_{\text{red}}$ ratio of 5/3 as shown in the following equations:

No distinction can be made between N_{ads} or $\text{NOH}_{\text{ads}}/\text{HNO}_{\text{ads}}$ as a coadsorbate with NO on the basis of the data in Table II. However, our IR measurements have shown that adsorbed NO could even be detected at low adsorbate coverages, and this strongly suggests that the $Q_{\text{ox}}/Q_{\text{red}}$ ratios of nearly unity at low adsorbate coverages are caused by a mixture of adsorbed N and NO. Moreover, the small reduction observed at 0.78 V in the cathodic scan after adsorption at open circuit potential from platinumoxide, supports the idea of NO dissociation into N and O. The possibility of NO dissociation being a cause of the high open circuit potential during adsorption has been mentioned by Langer and Pate⁴.

It is remarkable that, of the three basal planes of platinum, only the Pt(100) electrode is active in the formation of N_2O ¹⁴ in the liquid phase. Since this is the only plane active in the dissociation of NO at room temperature¹⁸, we conclude that N_2O formation proceeds through NO dissociation according to:

In UHV studies approximately 10 to 20% of the NO adsorbates on (100) sites dissociates at room temperature¹⁸. The experimentally obtained $Q_{\text{ox}}/Q_{\text{red}}$ ratio can be used to calculate the fraction of the adsorbate that consists of NO and of N species, using

$$\left(\frac{Q_{\text{ox}}}{Q_{\text{red}}}\right)_{\text{exp}} = f_{\text{NO}} \left(\frac{Q_{\text{ox}}}{Q_{\text{red}}}\right)_{\text{NO}} + f_{\text{N}} \left(\frac{Q_{\text{ox}}}{Q_{\text{red}}}\right)_{\text{N}}$$

$$f_{\text{NO}} + f_{\text{N}} = 1$$

where f_{NO} and f_{N} are the fractions of the adsorbate that consists of NO and N species, respectively. It follows from the previously given reduction and oxidation reactions of NO and N that $(Q_{\text{ox}}/Q_{\text{red}})_{\text{NO}} = 3/5$ and $(Q_{\text{ox}}/Q_{\text{red}})_{\text{N}} = 5/3$. The experiment with the highest adsorbate coverage was characterised by an $Q_{\text{ox}}/Q_{\text{red}}$ ratio of 0.75. From this experimentally derived ratio it can be calculated, using the equations given above, that 85% of the adsorbate consists of NO_{ads} and 15% consists of N_{ads} . The same value for $Q_{\text{ox}}/Q_{\text{red}}$ was also found for irreversible adsorbates formed from nitrate on polycrystalline platinum at a similar adsorption potential³². For the experiments with lower coverages the $Q_{\text{ox}}/Q_{\text{red}}$ ratio of approximately one indicate that the dissociated fraction increases. This means that, for low coverages, a higher dissociated fraction is found than the 10 to 20% reported in the UHV study on Pt(100). This might be due to the presence of sites with higher reactivity towards dissociation than Pt(100), such as stepped surfaces like Pt(310) and (410)¹⁸. Further, in our

case, the adsorbed oxygen atoms formed in the dissociation of NO are immediately reduced to water, enabling higher N_{ads} coverages to be formed.

It is possible to calculate the total adsorbate coverage from the experimental ratio $Q_{\text{ox}}/Q_{\text{red}}$, independent of the nature of the coadsorbate, N or NOH. The average number of electrons involved in the reduction or oxidation of a single adsorbate species, n_{red} and n_{ox} , can be derived using the experimentally found $Q_{\text{ox}}/Q_{\text{red}}$ ($= n_{\text{ox}}/n_{\text{red}}$) ratio in combination with $n_{\text{ox}} + n_{\text{red}} = 8$. The latter follows from the fact that the oxidation state of the adsorbate lies between -III, the value for NH_4^+ , and +V for NO_3^- . Since in the reduction and oxidation of the adsorbate the only products are NH_4^+ and NO_3^- , respectively it follows automatically that $n_{\text{ox}} + n_{\text{red}} = 8$. Having calculated the n_{red} and n_{ox} values from the experimental $Q_{\text{ox}}/Q_{\text{red}}$ ratio, the total adsorbate coverage θ_{tot} can be calculated using the relation $Q_{\text{red}} = Q_{\text{ox}}^{\text{H}} \theta_{\text{tot}} n_{\text{red}}$. Using this procedure the saturation coverage is found to be 0.41, corresponding with a reduction charge of 398 $\mu\text{C}/\text{cm}^2$. This value is somewhat lower than the saturation coverages of 0.46 and 0.51 reported for the Pt(110) and Pt(100) electrodes, respectively¹⁶.

It is remarkable that such a small amount of N_2O is formed in the double-layer region in the cathodic scan after adsorption. This potential-dependent behaviour may be caused by several factors. First, the IR experiments demonstrated a shift of the NO stretch vibration frequency upon changing the electrode potential. This shift, known as the Stark effect, is well known for CO; the shift of the CO stretch vibration to lower wavenumbers upon lowering the potential is explained by extra donation of charge from the $d\pi_{\text{Pt}}$ orbital to the $2\pi^*$ orbital of the CO molecule, resulting in a weakening of the C-O bond³³. At the same time, the M-C bond is strengthened, as indicated by a shift of the M-C stretch frequency to higher wavenumbers observed with Surface Enhanced Raman Spectroscopy (SERS)³⁴. The same potential-dependent metal-adsorbate bonding is at hand for adsorbed NO and the extra charge in the antibonding orbitals might trigger the dissociation of a fraction of the NO molecules. The dissociation may be followed by recombination of an N species with an NO molecule to give N_2O . The corresponding current that was observed can be ascribed to the immediate reduction of the O atom formed in the dissociation. A second factor that may explain the N_2O formation in the cathodic scan after adsorption is the effect of the electrode potential on the bonding strength of both coadsorbed water and sulfate anions. It is known from radiotracer experiments³⁶ and IR spectroscopy³⁷ that the coverage of sulfate anions increases at higher electrode potentials. Electrochemical Quartz Crystal Microbalance (EQCM) measurements show that simultaneous adsorption of sulfate anions and water molecules occurs^{38,39}. This means that the cathodic scan, recorded in fresh electrolyte after adsorption, is accompanied by a decreased ability for coadsorption of water and sulfate anions with decreasing potential and this may as well be responsible for the dissociation of some NO, leading to N_2O formation.

Conclusions

Infrared experiments have shown that adsorbed NO is present on the platinum electrode after exposure to NO-containing solutions. Vibrations characteristic of NO adspecies on (100) and (110) sites of platinum were observed. The presence of two separate reduction peaks in the cyclic voltammogram supports this conclusion. Evaluation of the charges involved in both the oxidation and reduction of the adsorbate layer leads to the conclusion that coadsorbates are present in addition to adsorbed NO. On the basis of our measurements, we conclude that the coadsorbates consist of nitrogen adatoms, formed by the dissociation of NO at room temperature. We

therefore propose that the electrochemical reduction of NO to $\text{N}_2\text{O}^{1-12}$ proceeds through dissociation of NO, followed by recombination of NO with N. This contrasts with the general view that N_2O formation proceeds through dimerization of adsorbed NOH or HNO species to $\text{H}_2\text{N}_2\text{O}_2$ followed by N_2O formation.

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