

Redox transformations of adsorbed NO molecules on Pt(100) electrode.

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Electrochemical behaviour of adsorbed NO molecules on Pt(100) electrode has been studied in perchloric acid solutions by means of cyclic voltammetry. According to literature data, saturated NO adlayer with coverage of ca. 0.5 ML is formed at open circuit conditions in nitrite solution as a result of disproportion reaction. The adlayer is stable in the range of 0.4-0.9 V, NO molecules are oxidized at 0.9-1.1 V and can be reduced to ammonia at potentials less than 0.4 V. Stability of the adlayer depends on surface coverage and extent of the ordering. Unsaturated NO adlayer demonstrates redox transformations $\text{NO} \leftrightarrow \text{NH}_3$ at 0.5-0.8 V.

Key words: Pt(100), nitrogen oxide NO.

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INTRODUCTION

Short review of the literature devoted to studies of kinetics and mechanism of electrochemical reactions with participation of nitrogen-containing substances are given in Refs. [1-3]. Attention to these processes does not wane due to its fundamental and applied importance. As the reduction of nitrogen-containing compounds is a structure-sensitive process, the investigations performed at single crystal electrodes are of greatest interest [1-3,18-35]. The use of the electrodes with clearly characterized surface structure allows revealing the correlations between electrochemical activity of adsorption sites and their structure.

The aim of this work was detailed study of kinetics and mechanism of redox transformations of NO molecules adsorbed on Pt(100) surface.

EXPERIMENTAL

The study was carried out using the technique of electrode surface preparation and cleaning developed in the works of Clavilier et al. [22–25]. The electrode Pt(100) with the working surface area of 0.035 cm² was obtained after orientation, cutting and polishing of spherical single crystals. The misalignment angle of the (100) crystallographic plane of single crystals from the real electrode surface did not exceed 0.1°.

The electrode was annealed for 20–40 s in the flame of a Bunsen burner before each experiment to remove impurities and to order the surface structure, cooled in an argon–hydrogen gas mixture (3:1). Then it was rinsed with water saturated by this mixture and transferred into a cell with 0.1 M HClO₄ degassed by argon. Then background CVs were recorded to control the cleanness of the system.

The measurements were carried out in glass cells with separate compartments for an auxiliary Pt electrode and reversible hydrogen reference electrode (RHE). The solutions were prepared on the basis of NaNO₂ и NaNO₃ (“p.a.”, Merck), HClO₄ and aqueous NH₄OH solution (suprapure grade, Merck) in Milli-Q water (Millipore) with specific resistance of 18 MOhm·cm and the content of organic impurities of less than 5 ppb. High-purity argon was used for solution deaeration, the inert gas was blown over the solutions in the course of the experiments. To introduce an additive of potassium nitrate or ammonium, the meniscus was broken and the electrode was left above the solution in an argon atmosphere. After adding an aliquot of the potassium nitrate or ammonia solutions, argon was bubbled through electrolyte for several minutes to level the additive bulk concentration and remove oxygen traces from the system. Then, a meniscus was formed, potential cycling was resumed, and CVs were registered.

A computer-controlled potentiostat and software developed in A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy of Sciences, were used for data registration and processing.

NO adlayers were formed in solutions of 0.05-500 mM NaNO₃ at open circuit [24,27-29,34]. The surface coverage θ_{NO} depends on the solution concentration and duration of the contact. Then the electrode was rinsed with water and transferred into a cell for electrochemical measurements.

RESULTS AND DISCUSSION

It's known that saturated NO adlayer on Pt(100) with coverage of ca. $\theta \approx 0.5$ ML is formed for enough long contact of the electrode with acidic solution of sodium or potassium nitrite at open circuit [24,27-29,34]. CVs in Fig. 1b were recorded after formation of saturated NO adlayer on Pt(100) for 100 s in 0.5 M NaNO₂ and rinsing the electrode with water.

During the rinsing, oxygen adsorption occurs, adsorbed oxygen is removed at the 1st negative-going potential sweep from 0.85 V (meniscus formation) to 0.6 V (curves 1), further potential cycling within 0.6-0.85 and 0.4-0.85 V demonstrates only recharging the double layer (curves 1,2), faradaic processes don't occur as adsorbed NO molecules impede adsorption of hydrogen, oxygen and solution components. In the range of 0.85-1.10 V redox peaks of NO \leftrightarrow NO₂⁻ process are observed [28].

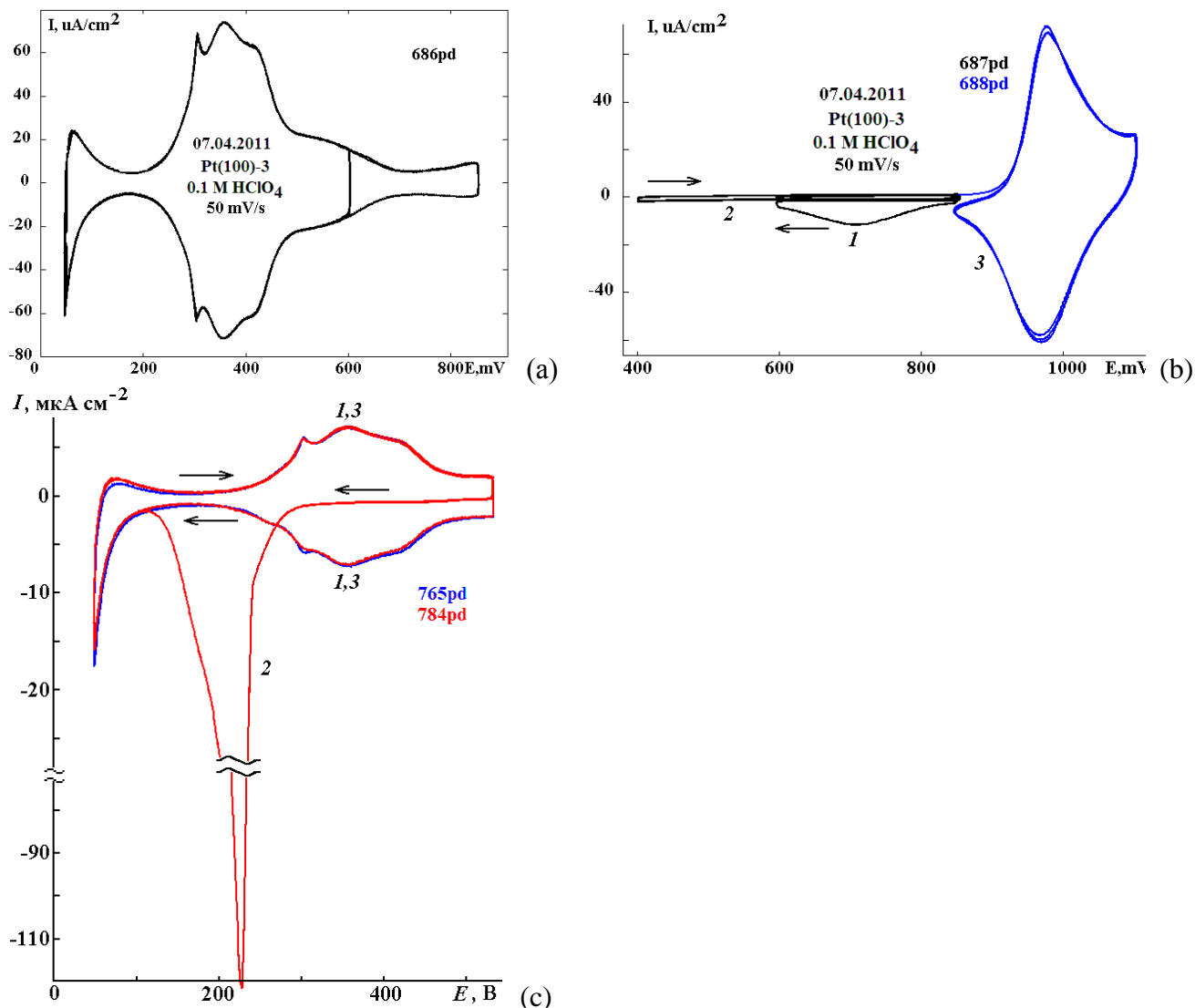
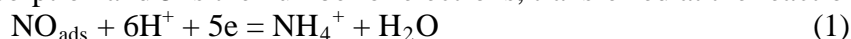


Fig. 1. CVs of Pt(100) in solution of 0.1 M HClO₄ at the potential sweep rate of 50 mV s⁻¹ (a,b) and 5 mV s⁻¹ (c). (a) Background curves with anodic limits of 0.60 and 0.85 V. (b) CVs after formation of saturated NO adlayer in solution of 0.5 M NaNO₂ and rinsing with water. *I* – CVs in the range of 0.60-0.85 V recorded immediately after meniscus formation at 0.85 V (start potential), curves 2 – 5 cycles 0.40-0.85 V, curves 3 – 3 cycles 0.85-1.10 V. (c) Background CV (*I*), the curve of NO reduction (2) during negative-going potential sweep and following cycle 0.05-0.50 V (3).

Complete removing of NO adlayer is occurred at negative-going potential sweep to 0.05 V at enough low sweep rate (NO reduction to ammonia starts at 0.3 V, ammonia is desorbed due to competitive adsorption of hydrogen) [24,27-29,34], further CVs correspond to practically clean Pt(100) surface (Fig. 1c). It means that there were no any noticeable oxidation and/or disordering of Pt(100) surface in the range of 0.85-1.10 V. Estimation $\theta_{\text{NO}}=0.48$ ML for this experiment was done by integration of negative-going potential sweeps of curves *I* and 2 in Fig. 1c, the difference of the charges was divided by $210 \cdot 5=1050 \mu\text{C cm}^{-2}$, where $210 \mu\text{C cm}^{-2}$ is the charge of monolayer adsorption and 5 is the number of electrons, transferred at the reaction



occurring.

Partially reduced NO adlayer loses its stability in the potential range of 0.50-0.85 V and electrochemical transformations of adsorbed NO molecules take place as shown in Ref. [27]. In this study, saturated NO adlayer was partially reduced during potential excursion from 0.50 to 0.22 V and back. During following potential cycling between 0.50 and 0.87 V anodic peak at 0.78 V and cathodic one at 0.6 V were observed (similar to presented in Fig. 2b), these peaks decreased with time of the cycling. Only assumptions concerning a nature of the redox process were made because concrete conclusions demanded additional investigations. CVs of partial reduction of saturated NO adlayer

(negative-going potential sweep from 0.85 to 0.25 V at 5 mV s^{-1} , positive-going sweep back to 0.85 V at 50 mV s^{-1} , curves 2 and 3, respectively) and following potential cycling between 0.50 and 0.85 V (10 cycles at 50 mV s^{-1}) are presented in Fig. 2a. It was reduced of ca. 0.08 ML of NO_{ads} (integration of curves 2 and 3, reaction (1), cathodic charge $63+17=80 \mu\text{C cm}^{-2}$), consequently, before the cycling within 0.50-0.85 V, about 0.4 ML of NO_{ads} were remained on the surface. It should be noted that charge of hydrogen adsorption (this process occurs simultaneously with NO reduction) was not taken into account therefore the value $\theta \approx 0.08$ is overestimated.

There are two smooth peaks in CV 3 (Fig. 2b). The first one is observed at 0.50-0.65 V (maximal current of $1.3 \mu\text{A cm}^{-2}$ at 0.57 V, hydrogen desorption) and second - at 0.65-0.80 V (maximal current of $10.2 \mu\text{A cm}^{-2}$ at 0.77 V). Enhanced currents at 0.80-0.85 V in curve 3 (as compared with currents of curves 1, which are characteristic for recharging of double layer at the electrode with saturated NO adlayer) are mainly due to oxygen adsorption. One can see that these currents are lower than those of background CV 7 for clean Pt(100) electrode as a part of surface is blocked with adsorbed NO.

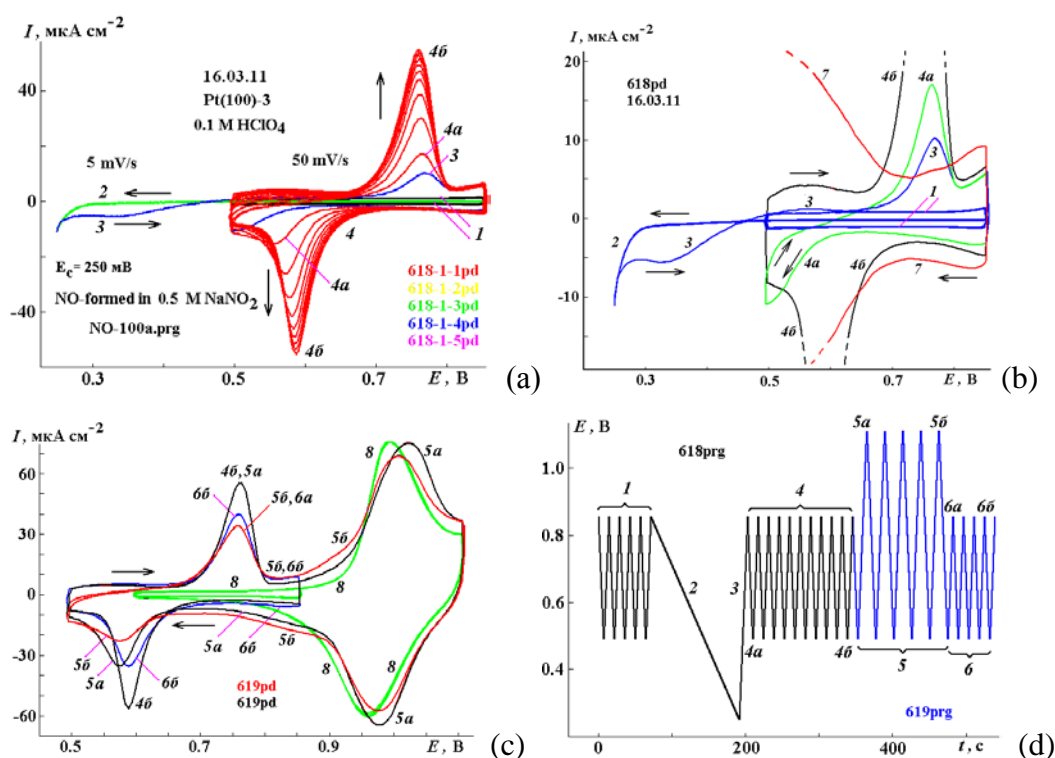


Fig. 2. CVs of Pt(100) with NO adlayer in solution of 0.1 M HClO_4 . (a) Curves 1 – 5 cycles of the adlayer stabilization in the range of 0.50-0.85 V, curves 4 – 10 cycles 0.50-0.85 V, vertical arrows point to changes in the peak height during potential cycling. 4a – 1st and 4b – 10th cycles. (b) Curves 1-4 and fragment of background CV (7) in enlarged scale. (c) 4b – 10th cycle 0.50-0.85 V, 5a,5b – 1st and 5th cycles 0.5-1.1 V, respectively, 6b – 5th cycle 0.50-0.85 V, 8 – CV of Pt(100) with saturated NO adlayer. (d) Scheme of electrode polarization program. The potential sweep rate are 5 mV s^{-1} (curve 2 in Fig. 2a) and 50 mV s^{-1} (all others). See explanations in the text.

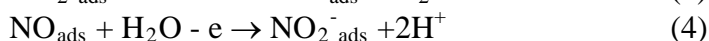
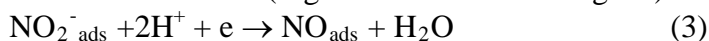
During the potential cycling between 0.50 and 0.85 V, the currents first grow but after 8-9 cycles are stabilized. At 0.50-0.65 V, small amount of hydrogen is desorbed at positive-going sweeps, and at 0.65-0.80 V an anodic peak is observed. One of the aims of this study is the ascertaining of nature of the peak. At negative-going potential sweeps cathodic counter-peak is observed at 0.6 V, the charge of this peak Q_c is close to that of anodic peak Q_a . For instance, for 10th cycle (curve 4b in Fig. 2) $Q_a=69 \mu\text{C cm}^{-2}$ (0.64-0.82 V) и $Q_c=75 \mu\text{C cm}^{-2}$ (0.74-0.50 V). The difference in the charges could be due to some uncertainty of choose of integration range and contribution of adsorption/desorption of oxygen and hydrogen. However, the similarity of the Q_a and Q_c values gives the base to consider that some adsorbed substance N_x , (formed at NO reduction), is oxidized to N_y during positive going potential sweeps. After the sweeping reverse, the opposite reaction occurs. So that, redox couple



is realized at 0.5-0.8 V for partially reduced saturated NO adlayer.

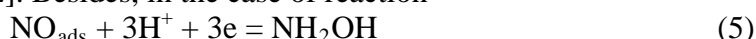
According to Refs. [24,27-29,34], the main product of adsorbed NO reduction at Pt(100) is the ammonia. Formation of N₂O is rather improbable as this product was detected only in the presence of dissolved NO in the solution [26, 32]. N₂O was not observed in the case of NO reduction on Pt(100) and in situ control of the surface by IR-spectroscopy [30]. It was shown in Ref. [31] that in nitrate-containing solutions anodic peak at 0.78 V corresponds to NH₃ or NH₂OH oxidation to NO or NO₃⁻. However, the nitrate reduction to NO occurs at 0.7-0.8 V during negative-going potential sweep (the peak centered at 0.74 V) but not at 0.6 V (Fig. 2). Hence, one should consider N_y=NO as a most probable product of N_x oxidation.

It's known [28] that for saturated ordered NO adlayer, oxidation of NO to NO₂⁻ and opposite reaction occur at 0.9-1.1 V (Fig. 1b and curve 8 in Fig. 2c).



After registration of CVs presented in Figs. 2a and 2b, anodic(upper) limit of potential cycling was increased to 1.1 V and CVs 5 were obtained (Fig. 2c), which are characteristic for Pt(100) with NO adlayer. Redox peaks at 0.95-1.0 V decreased slightly during the cycling, this is due to slow desorption nitrogen-containing substances, which participate in reactions (2)-(4), and corresponding decrease of NO_{ads} amount. It should be noted that enhanced currents (as compared with CVs for saturated NO adlayer, curve 8) are observed between the peaks of redox processes, these currents are due to oxygen adsorption/desorption on platinum with loose NO adlayer. For the negative-going potential sweep of the 1st cycle 0.5-1.1 V (curve 5a) these currents are lower than those for 5th (curve 5b). This fact is also evidence of decrease in adsorbate amount during the potential cycling with high anodic limit of 1.1 V. Contribution of oxygen adsorption/desorption takes place as well in the potential range of redox processes (3,4) occurring.

When we try to ascertain the origin of the substance N_x, following facts have to be taken into account. As it was shown in Refs. [24,27-29,34], reduction of saturated NO adlayer occurs at 0.1-0.3 V (Fig. 1c) with formation of ammonia. Unfortunately, IR-spectroscopy does not allow discerning hydroxylamine and ammonia, as the adsorption band at 1480 cm⁻¹ may be attributed to the both substances [22]. Use of individual substances, i.e., NH₂OH and NH₃ adsorbed on platinum, yields no intended effect as they undergo electrochemical transformations in a wide range of potentials. For instance, reduction of NH₂OH to NH₃ and oxidation of NH₂OH to NO occurs between 0.1 and 0.8 V [22]. Besides, in the case of reaction



the charge would correspond to θ_{NO}=0.8 ML, this value is too high for saturated NO adlayer, it does not agree with estimations, which were done on the base of spectroelectrochemical measurements [34] and UHV studies [*Gardner P., Tiishaus M., Martin R., Bradshaw A.M. // Surf. Sci. 1990. V. 240. P. 112.*]. Therefore, one should consider ammonia or ammonium ions as a substance N_x.

It is worth to note that the currents of NO reduction and N_x oxidation at 0.5-0.8 V decreased as well (compare curves 4b, 5a and 5b in Fig. 2c). Apparently, this effect is due to decrease in adsorbate amount, influence of oxygen coadsorbed with NO (NO reduction could be hindered or slowed in the presence of oxygen), and disordering the Pt(100) surface structure at its oxidation.

After 5 cycles 0.5-1.1 V, anodic limit of the cycling was lowered to 0.85 V (curves 6 in Fig. 2c, the positive-going sweeps of the CVs 5b and 6a practically coincide), the peaks of redox reactions (2) slightly increased and "oxygen" currents at 0.80-0.85 V decreased (compare the curves 5b and 6b in Fig. 2c). This fact indicates that decrease of peaks in CV 5 can't be explained only by decrease in amount of the adsorbate.

Let us discuss some additional results on a behaviour of partially reduced saturated NO adlayer. CVs recorded before (curves 1) and after potentiostatic treatment (curves 2,3) of saturated NO adlayer at 0.25 or 0.30 V for 100 s are shown in Fig. 3a. The electrode conditioning at 0.35 V does not change the state of the adlayer, its reduction or oxidation does not occur in the range of 0.50-0.85 V, no any redox peaks are observed. Current transients of NO reduction at 0.25 or 0.30 V are presented in Fig.3b.

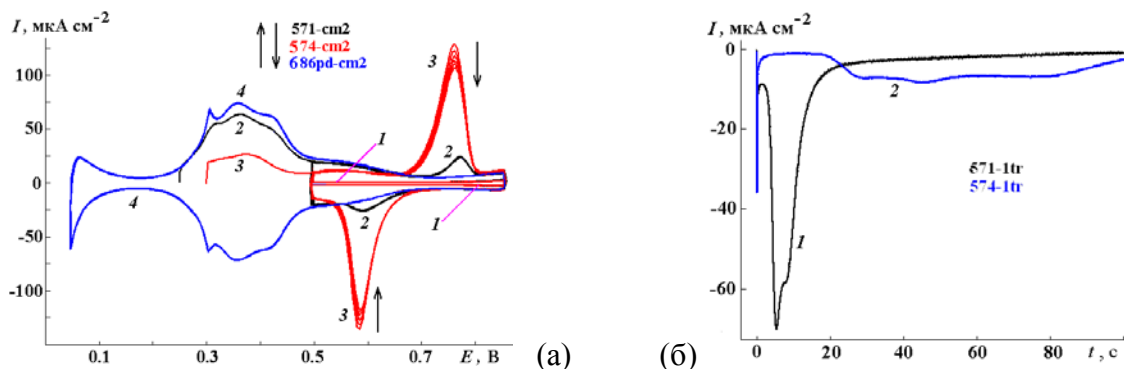
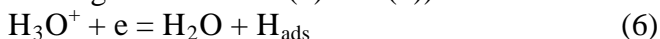
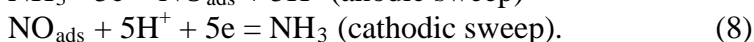
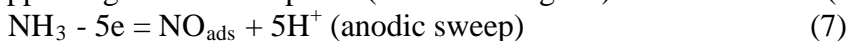


Fig. 3. (a) CVs of Pt(100) with NO adlayer in solution of 0.1 M HClO₄. 1 – 5 cycles of the adlayer stabilization in the range of 0.50-0.85 V, (2,3) – positive-going potential sweep after conditioning of Pt(100) with saturated NO adlayer for 100 s at 0.25 (2) or 0.30 V (3) with following 5 cycles 0.50-0.85 V. Vertical arrows point to changes in the peak height during potential cycling. 4 – background CV. The potential sweep rate is 50 mV s⁻¹. (b) Potentiostatic current transients of Pt(100) with saturated NO adlayer recorded during conditioning at 0.25 (1) or 0.30 V (2).

The estimations of reduced NO amounts were done by means of integration of current transients (total charge of reactions (1) and (6))



and positive-going sweeps from the potentials of the conditioning to 0.65-0.70 V (curves 2,3 in Fig. 3a, the charge of hydrogen desorption), the difference of the charges was divided by 210·5=1050 μC cm⁻². It turned out, that in both cases approximately the same amount of NO (about 0.4 ML) was reduced. However, almost twice more hydrogen was adsorbed at 0.25 V as compared with 0.3 V (curves 2,3 in Fig. 3a). Respectively, more ammonia was displaced from the platinum surface at 0.25 V. Let's remind that during negative-going potential sweep to 0.05 V practically complete reduction of NO and the ammonia desorption occur (Fig. 1c). As a result, the conditioning at 0.25 V for 100 s leads to appearing small redox peaks (curve 2 in Fig. 3a) of the reactions (7) and (8)



After the treatment at 0.3 V noticeable redox peaks are observed in CVs 3, they slowly decreased with time of the cycling. One can conclude that value of the peaks is determined not only remaining θ_{NO} but also the amount of coadsorbed ammonia. Apparently, the decrease in peak height is due to slow desorption of an adsorbate.

One can see (Figs. 2a, 3a) that electrochemical behavior of unsaturated (incomplete) NO adlayer considerably depends on coverage θ_{NO} at the beginning of negative-going potential sweeps and probably on the extent of its ordering. The redox peaks can grow, decrease or be stable for some period of time (Figs. 2a, 3a and Ref. [27]).

CVs of Pt(100) in the presence of ammonium ions are shown in Fig. 4. One can see that at $E < 0.7$ V the ammonium ions are weakly adsorbed on platinum (they can't compete with hydrogen adatoms) and are not undergone to noticeable electrochemical transformations: the shape of CV profiles in the presence of ammonia slightly differs from background CV of Pt(100) in 0.1 M HClO₄. However, an increase of the upper limit of potential cycling leads to appearing the redox peaks, oxidation of ammonia occurs at 0.7-0.8 V and opposite process is observed at negative-going potential sweeps at 0.55-0.70 V (curve 4 in Fig. 4a). Comparison of CVs presented in Figs. 3 and 4 shows that adsorbed ammonia is undergoing to similar transformations as product of partial reduction of saturated NO adlayer.

The potential cycling between 0.50 и 0.85 V leads to growth of the redox peaks during first 15-20 cycles, then CV profile is stabilizing (Fig. 4b). The charges of anodic and cathodic potential sweeps are practically the same and correspond to reactions (7) and (8) (at high potentials adsorption of ammonium ions on positively charged platinum surface seems to be less probable than that of neutral ammonia molecules) with participation of ca. 0.15 ML of ammonia or NO (this value is overestimated as the double layer recharging was not taken into account). Cathodic peak at 0.6 V corresponds to the

reaction of NO reduction, it is characteristic for small amount of disordered adsorbate [27]. The increase in height and charge of the peaks during the potential cycling between 0.50 and 0.85 V (Fig.4b), apparently, is due to slow accumulation of NO_{ads} on the platinum surface and corresponding increase of coadsorbed ammonia.

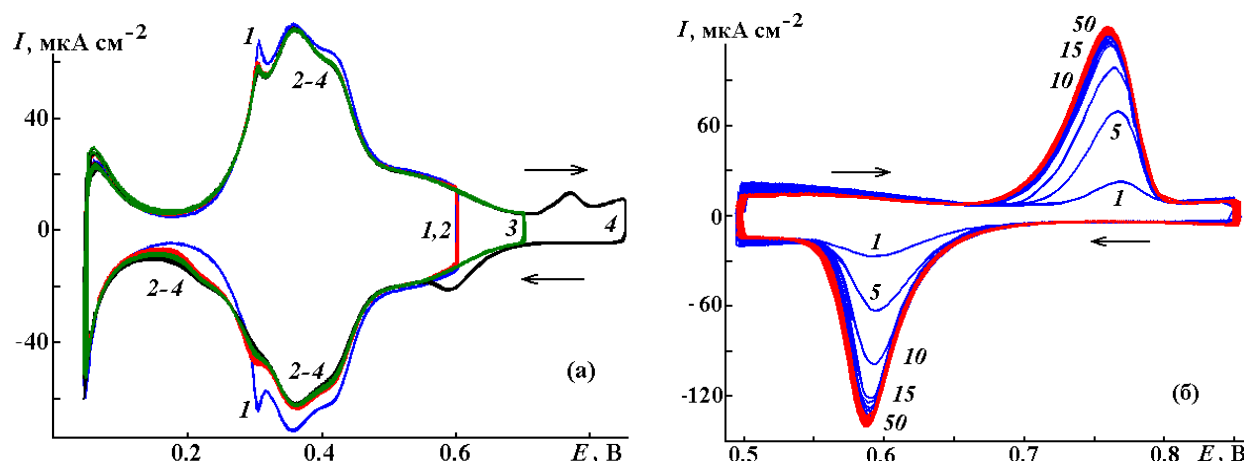


Fig. 4. CVs of Pt(100) at 50 mV s^{-1} in the solutions of 0.1 M HClO_4 (curve 1 in Fig. 4a) and 0.1 M $\text{HClO}_4 + 5 \text{ mM NH}_4\text{OH}$. (a) CVs with variable anodic limit E_a , V: 2 - 0.60, 3 - 0.70, 4 - 0.85. (b) 50 cycles of 0.50–0.85 V, the numbers near the curves correspond to numbers of successive cycles.

Now it is necessary to understand why the peaks grow during the potential cycling between 0.5 and 0.85 V after partial reduction of saturated NO adlayer (Fig. 2a). Let's remind that about 0.4 ML of NO and some amount of coadsorbed ammonia were present on the platinum surface. At the end of positive-going sweep from 0.25 to 0.85 V (curve 3) the ammonia was oxidized to NO (the charge of anodic peak corresponds to oxidation of ca. 0.02 ML of NH_3 , a part of the product was displaced by hydrogen adatoms. The adlayer became less dense but one can assume that it consisted from ordered 2-dimensional domains divided by areas of disordered adsorbate. In this case the rate of NO reduction at negative-going potential sweeps should be higher at the perimeter of the domains and between them. During the cycling at rather high sweep rate, one can expect gradual decrease of the domain size, increase of their amount (fragmentation) and expanding the areas of disordered adsorbate (Fig. 5a) because NO molecules formed as a result of the ammonia oxidation have not enough time to build in the ordered domains. This scheme allows explaining the growth of the redox peaks during the cycling (Fig. 2a). However, the peak growth can't continue for infinite period of time, at some moment a steady-state conditions will be realized and later the peak height will decrease due to slow adsorbate desorption. This effect is observed experimentally for not very high initial coverage θ_{NO} (curve 3 in Fig. 3a) or long-term potential cycling (Fig. 5c).

A gradual decrease of θ_{NO} for Pt(100) with saturated ordered NO adlayer can be provided during the potential cycling at relatively high sweep rate (50 mV s^{-1}) in the range of 0.25-0.85 V. During the every cycle a small amount of NO is reduced and amount of the adlayer defects gradually increased. CVs of this experiment are shown in Figs. 5b, 5c. After meniscus formation for the electrode with saturated NO adlayer, the cycling between 0.85 and 0.50 V was started to stabilize (ordering) the adlayer, further lower limit of the cycling was decreased to 0.3 V (10 cycles, there was no noticeable NO reduction) and 0.25 V. During several cycles (from 3 to 8 for several similar experiments, it depends on quality of flame annealing and cooling of Pt(100), duration of the electrode rinsing after its contact with nitrite solution, duration of the adlayer stabilization etc., for given experiment it were 1st-3rd cycles 0.85-0.25 V) the only indication of NO reduction was slight increase of cathodic currents at 0.25-0.30 V. Then the currents grew abruptly (5th cycle), the redox peaks appeared and increased in height. CV profiles with maximal redox peaks were observed for 7th-8th cycles. Further cycling leads to desorption of the adsorbate (currents of hydrogen adsorption/desorption at 0.25-0.50 V grow) and corresponding decrease of the redox peaks at 0.50-0.85 V. It looks like there is some critical θ_{NO} coverage, at which disordering of the adlayer starts and it loses stability.

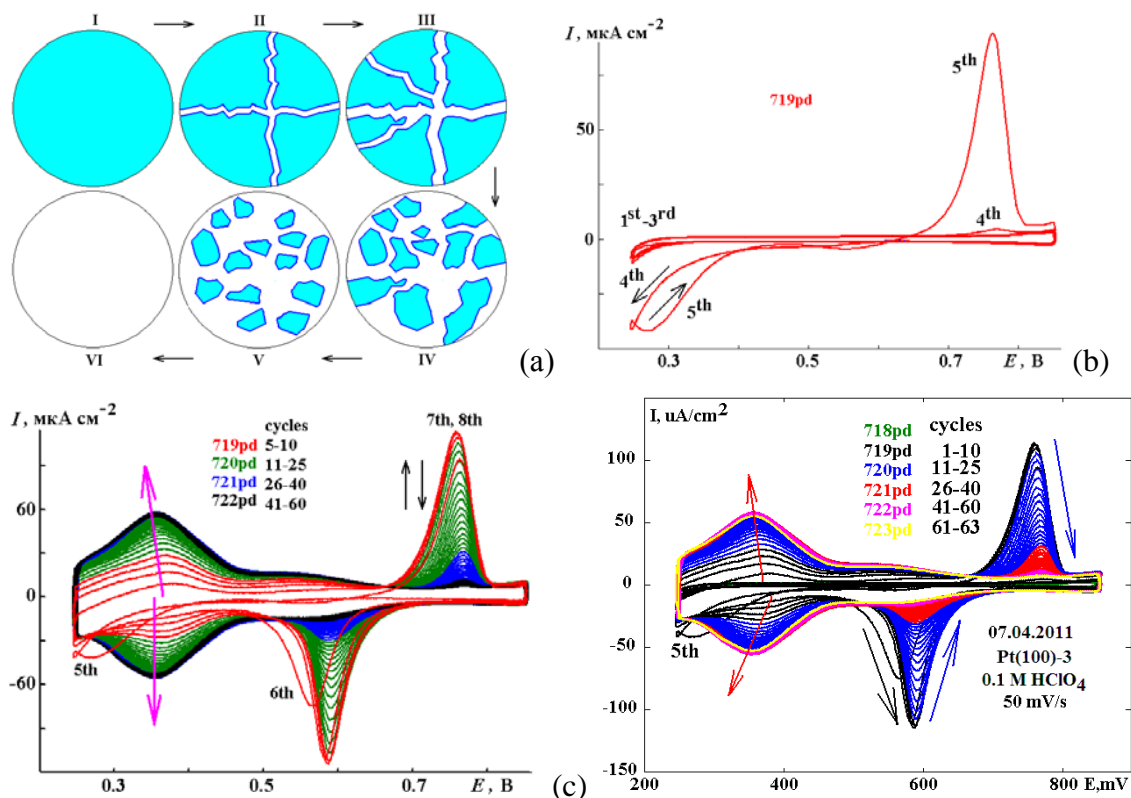


Fig. 5. (a) The scheme of reduction of saturated NO adlayer. I – ordered adlayer, II-V – appearing the boundaries between the domains and expanding the areas of disordered adsorbate, VI – disordered adlayer. (b) Beginning the experiment, 1st-5th cycles of Pt(100) with saturated ordered NO adlayer. (c) The following 55 cycles. Sweep rate is 50 mV s^{-1} , solution of 0.1 M HClO_4 .

Incomplete NO adlayer could be obtained by partial reduction of the saturated adlayer or by contact of the electrode with diluted nitrite solution where NO adsorption is a diffusion-controlled process. The latter manner allows avoiding the presence on the surface of the product of NO reduction coadsorbed with remaining NO molecules. In this case, only NO_{ads} is present on the surface at the beginning of the 1st negative-going potential sweep from 0.8 to 0.5 V. CVs for the Pt(100) electrode with incomplete NO adlayer formed at open circuit in solution of 0.05 mM NaNO_2 for 7-10 s are presented in Fig. 6. The meniscus was formed at 0.8 V to minimize the oxidation and disordering of the Pt(100) surface.

First, a stabilization of incomplete NO adlayer (curves 2) was performed in the range of 0.7-0.8 V. The currents are considerably higher as compared with those of saturated adlayer (curves 1) due to oxygen adsorption/desorption. Further, negative-going potential sweep from 0.8 to $E_c=0.05 \text{ V}$ at 5 mV s^{-1} (curve 3) was applied to reduce NO and estimate the surface coverage, $\theta_{\text{NO}} \approx 0.18 \text{ ML}$ was obtained with account of hydrogen adsorption (curve 4). The following potential cycling between 0.5 and 0.8 V (curves 5) has not shown any redox peaks because the product of NO reduction (ammonia) was completely displaced by adsorbed hydrogen.

Similar experiment was carried out for $E_c=0.5 \text{ V}$ (curve 6 is practically coincides with curve 3 at 0.5-0.8 V) to minimize ammonia displacement by hydrogen adatoms. One can see that a redox couple has appeared after NO reduction (curves 7), the peaks decreased slowly due to adsorbate desorption (the anodic currents of hydrogen desorption at 0.50-0.65 V grew gradually with time of the cycling). For the first cycle between 0.5 and 0.8 V, the charge of the anodic peak (0.62-0.80 V) corresponds to surface coverage of adsorbed ammonia of ca. 0.12 ML. It should be noted that about 0.08 ML of hydrogen was desorbed at 0.50-0.62 V (curves 7, first cycle). Although the estimations were done without double layer correction, the correlation of anodic and cathodic charges can be considered as satisfactory one.

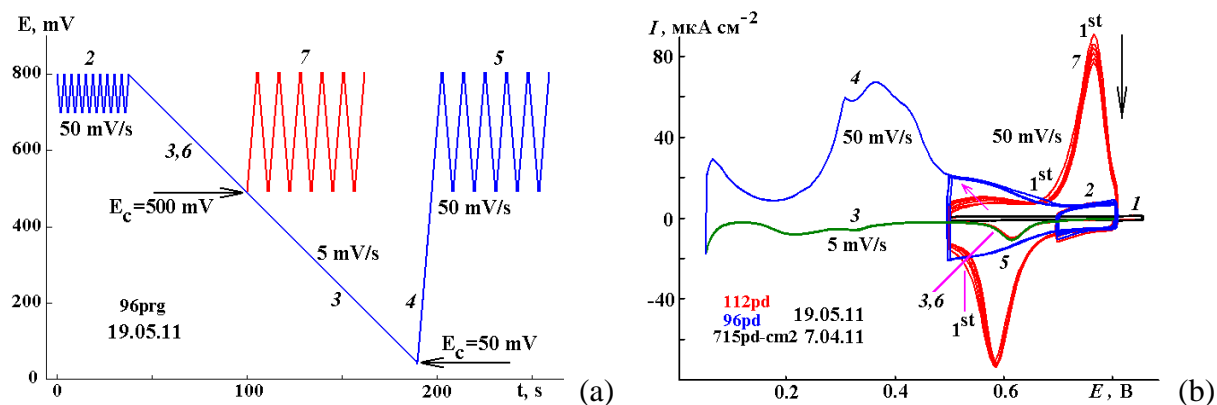


Fig. 6. (a) The schemes of polarization program. (b) CVs of Pt(100) electrode with saturated (1) and incomplete (2-7) NO adlayer. (1,2) – 10 cycles of stabilization of NO adlayer. Negative-going potential sweeps from 0.85 to 0.05 (3) and 0.50 V (6) at 5 mV s^{-1} . (4) – positive-going potential sweep of hydrogen desorption with following cycling between 0.85 and 0.50 V (5). (7) – redox peaks appeared after NO reduction.

CONCLUSIONS

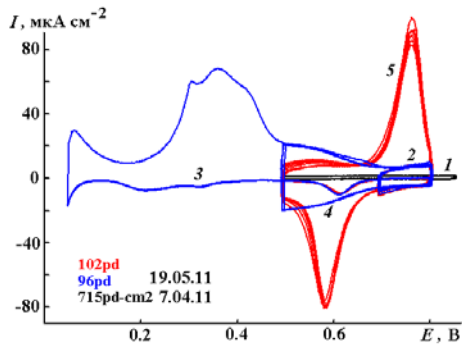
Performed studies allow to conclude that in contrast to stable saturated ordered NO adlayer on Pt(100) electrode with $\theta_{\text{NO}} \approx 0.5 \text{ ML}$, the surface redox processes $\text{NO}_{\text{ads}} \leftrightarrow \text{NH}_3_{\text{ads}}$ occur within incomplete NO adlayer (lowered coverage was obtained by partial NO reduction or NO adsorption from diluted nitrite solution) at potentials 0.5-0.8 V. Stability of the NO adlayer and intensity of oxygen coadsorption depend on surface coverage and extent of the ordering. The scheme of the ordered NO adlayer reduction has been suggested.

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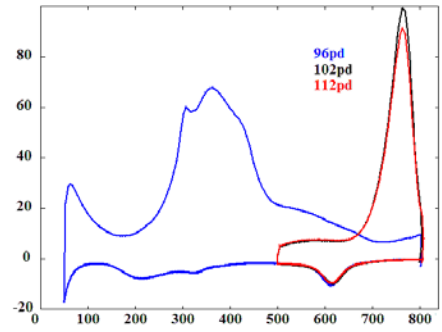
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similar experiment



Similar data were obtained in the presence of ammonia (704-713pd) or nitrate (732-743pd).

