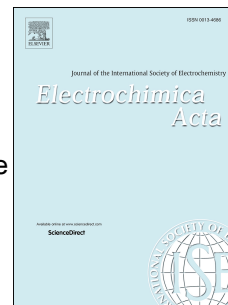


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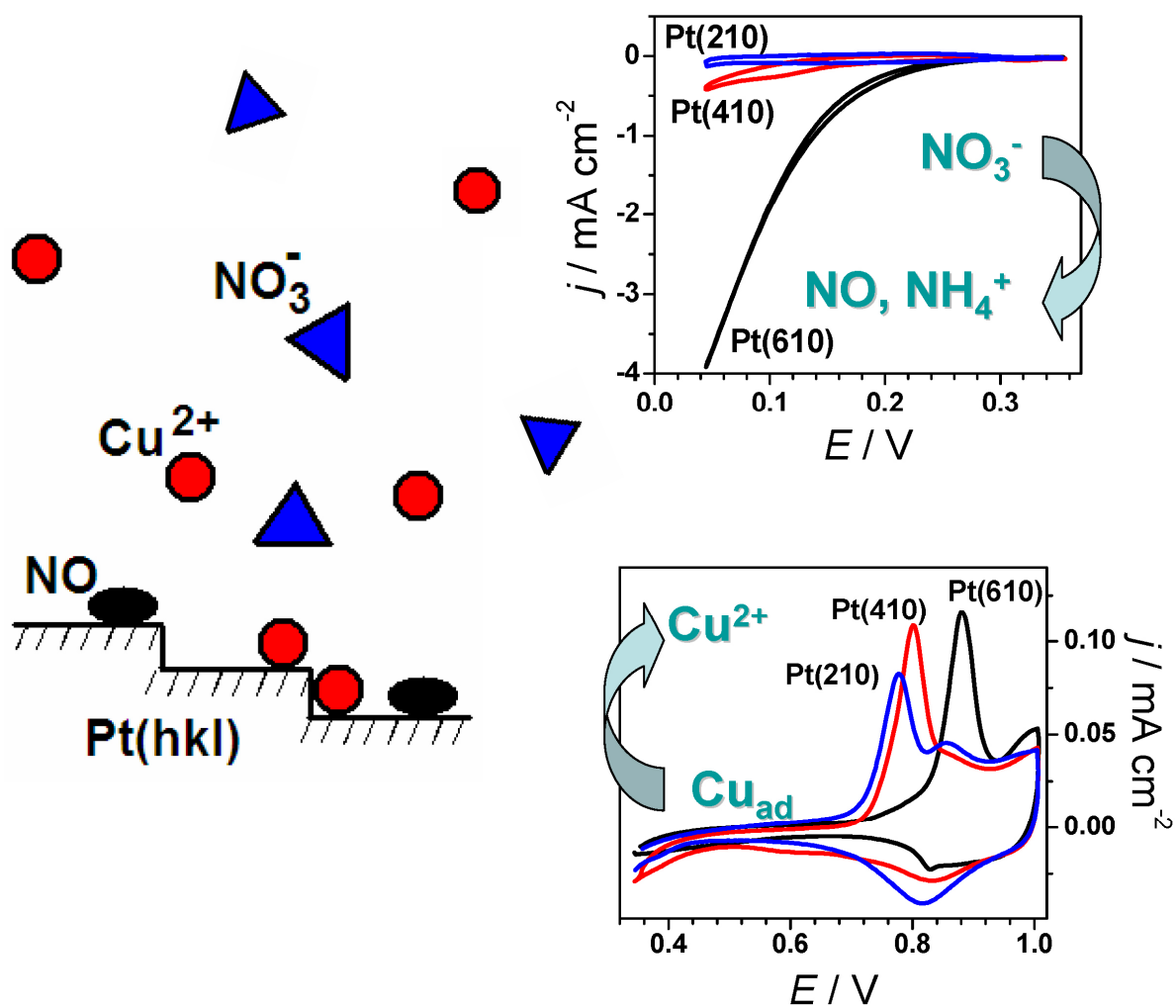
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Regularities of Nitrate Electroreduction on Pt(S)[n(100)x(110)] Stepped Platinum Single Crystals Modified by Copper Adatoms

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Abstract

Nitrate electroreduction is studied on Pt(S)-[n(100)x(110)] stepped platinum single crystals with 2, 4, and 6 atoms wide terraces modified by copper adatoms. The electrodes were modified by electrodeposition of Cu_{ad} in a 0.1 M HClO₄ + 0.020 M NaNO₃ + 10⁻⁵ M Cu(ClO₄)₂ solution by cycling the potential in the range of 50-350 mV, simultaneously with nitrate reduction. The peak of dissolution of copper adatoms in the nitrate solution is shifted in the positive direction, as compared to the nitrate-free solution, due to the stabilization of copper adatoms by adsorbed NO. This shift is not observed for Pt(210) with the terrace width of only 2 atoms: an increase in the terrace width results in the growing peak shift. The rate of nitrate electroreduction on modified electrodes increases by up to two orders of magnitude and grows at low copper coverages at an increase in the terrace width in the sequence of Pt(210) < Pt(410) < Pt(610). An increase in the surface coverage by copper adatoms causes redistribution of adatoms in the adsorption layer. In this case, the differences in the nitrate reduction rate decrease, but the sequence of Pt (210) < Pt (410) < Pt (610) is still preserved. The full surface coverage by Cu_{ad} cannot be obtained in this working solution by potential cycling in the range of 50–350 mV.

Key words: Pt stepped single crystals; electrocatalysis; copper-modified electrodes; nitrate electroreduction.

Introduction

The process of nitrate electroreduction on different electrodes has for many years been attracting active attention of researchers. This is due both to scientific (study of a multistage reaction, interest towards intermediates) and practical (water treatment) aspects. As found in [1-6], the final product of nitrate electroreduction on platinum group metals at potentials close to hydrogen evolution is ammonia. D. Pletcher et al. [7] showed that the nitrate ion is also reduced to ammonia on Cu in acidic media at a high rate. Gaseous NO was also found in the course of nitrate electroreduction on copper electrodes [8]. This was explained by the weakness of the bond between NO and the surface; no N₂O was detected. Nitrous oxide was found on polycrystalline Pd with a full monolayer of underpotentially deposited Cu. Let us point out that, as follows from the data of [9, 10], nitrous oxide is formed when NO is present in the solution.

Appearance of techniques of manufacturing electrodes with well defined single crystal surfaces of different orientation [11-13] gave new momentum to the understanding

of nitrate electroreduction. Studies on such electrodes allow establishing correlations between the structure of adsorption sites and their reactivity [14-19].

Selectivity, i.e., the reaction rate and products, can be changed by electrode surface modification by foreign metals. In situ FTIRS [20] showed that nitrate electroreduction on Pt(100) modified by a copper adlayer yielded nitrous oxide N_2O in perchloric acid solution, while the main product in sulfuric acid solution was ammonia.

Our previous studies on nitrate electroreduction on Pt(111) and Pt(111)+Cu electrodes [21] showed that the reaction in perchloric acid solutions occurred much faster on copper-modified Pt(111) surfaces than on pure Pt(111). The catalytic effect of copper adatoms is mainly due to the enhancement of nitrate adsorption (induced adsorption), as copper adatoms have a partial positive charge [22].

The electrode surface composition can be modified by a foreign metal deposit formed either at underpotential (upd) or at overpotential (opd). As shown in [23], deposition of phase copper on polycrystalline platinum occurs according to the Stransky-Krastanow mechanism: first, an upd monolayer is formed and then 3D crystallites grow on this layer. In the case of Pt(100) and single crystal electrodes with (100) terraces, there is a 2D phase copper layer in addition to the upd monolayer [24]; as the overpotential increases, 3D nuclei are formed on this 2D layer.

The reactivity of platinum substrates modified by monolayer and submonolayer amounts of copper adatoms is of great interest. A full copper monolayer forms a $Cu(1 \times 1)$ lattice on the Pt surface, i.e. there is a single copper atom per single platinum atom. Formation of an adlayer on platinum single crystals depends on the support structure. Previously, adsorption of Cu adatoms at Pt(S)[n(100)x(110)] and Pt(S)[n(100)x(111)] stepped single crystal Pt faces ((100) terraces of different width separated by parallel monoatomic steps with the (110) or (111) orientation, respectively) has been studied in solutions with strongly adsorbed anions: sulfate or chloride. Analysis of the changes in the shape of the "hydrogen region" in the course of copper accumulation from dilute solutions [25] shows that at the initial stages (at low surface coverages by copper adatoms, Θ_{Cu}) copper is adsorbed almost simultaneously on the (100) terraces and (110) steps. In [26], it is concluded that copper adatoms are deposited on stepped faces with (100) terraces and (111) steps predominantly on terraces and not on the steps.

In the absence of strongly adsorbing anions [27], copper adatoms on Pt(S)-[n(100)x(110)] at first fill both the steps and the terraces. As the surface coverage increases, islands of adatoms are formed and the peak potential of their dissolution is shifted to higher positive values. This effect is especially pronounced on Pt(100).

The aim of this work is to study the kinetics of nitrate anion electroreduction on the Pt(S)-[n(100)x(110)] faces from a solution also containing Cu^{2+} ions. It will be shown that modification of these electrodes by copper adatoms results in a significant acceleration of electroreduction of nitrate anions as compared to unmodified electrodes. In addition, the catalytic activity depends on the platinum surface structure (terrace width).

The products obtained in the course of nitrate electroreduction on various faces of unmodified and modified platinum have already been determined in a number of works [20, 28-31]. The attribution of the corresponding peaks in this paper is performed on the basis of the data obtained in these works.

EXPERIMENTAL

Electrodes with the working surface area of 0.03–0.04 cm^2 were made from single crystal beads, following the method of Clavilier et al. [11, 12, 32, 33].

Before every experiment, the electrodes were annealed in the flame of a Bunsen burner for 20–40 s to remove impurities and order the electrode surface structure. Then they were cooled in an argon–hydrogen gas mixture with the ratio of 3:1 and dipped into Milli-Q water saturated by this mixture. Then they were transferred, with a water drop to protect the surface from impurities, into a cell with 0.1 M HClO_4 solution purged by argon. A meniscus was formed at the electrode/solution interface (in the "hanging meniscus configuration", the solution contacts only the working single crystal face [34]) and cyclic voltammograms (CVs) were registered to control the purity of the solution and the quality of the annealing/cooling step on the electrode surface.

The measurements were carried out in glass cells with separate compartments for the auxiliary Pt electrode and the reversible hydrogen reference electrode in 0.1 M HClO_4 (RHE). The solutions were made of CuO and NaNO_3 (p.a., Merck) and HClO_4 (suprapure, Merck) using Milli-Q water with a specific resistance of 18 $\text{M}\Omega\text{cm}$ and a content of organic impurities lower than 5 $\mu\text{g/l}$ (ppb). Also, only this water was used for washing the

cells and the electrodes. High-purity argon was used for solution deaeration; the inert gas was blown over the solutions in the course of the experiments.

After testing the purity of the system, nitrate was added to the acid solution and the corresponding reference CVs were registered. Then a copper aliquot was added and a standard CV was recorded in the working solution ($0.1 \text{ M HClO}_4 + 0.02 \text{ mM NaNO}_3 + 10^{-5} \text{ M Cu}(\text{ClO}_4)_2$). During the addition of nitrate and copper aliquots, the electrode was placed above the solution in the stream of argon and the final solution was additionally purged by argon. The experimental procedure used to study nitrate electroreduction was as follows: once the electrode was immersed at 0.85 V , N cycles of accumulation of copper adatoms were recorded in the range of $350\text{--}50 \text{ mV}$ and nitrate reduction currents were registered. Then, two scans of copper dissolution in the range of $350\text{--}1000 \text{ mV}$ were recorded and the further two scans in the range of $350\text{--}850 \text{ mV}$ were registered for the leveling of the nearelectrode concentration of copper ions. This procedure was repeated several times for different N . When many copper accumulation cycles were applied, there was always an experiment with a small number of accumulation cycles (usually $2\text{--}5$, which allowed time for the leveling of the concentrations in the nearelectrode layer and the solution bulk). These curves were also used to check the reproducibility of the experiment. It should be noted that such a high potential of copper dissolution as 1000 mV is a necessary measure, because, as shown below, at lower potentials Cu adatoms cannot be removed from the platinum surface in the nitrate solution. No visible changes in the surface structure occur in the course of the experiment.

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.

In the figures, all potentials are given vs. the reversible hydrogen electrode. The potential sweep rate in all CVs is 50 mV s^{-1} .

RESULTS AND DISCUSSION

Standard CVs in perchloric acid solution

In this work, Pt(610), Pt(410), Pt(210) single crystal electrodes with (100) terraces of different width separated by monoatomic steps with the (110) orientation were used.

Standard CVs of the electrodes in perchloric acid are shown in fig. 1a. The electrode surface structure is schematically shown in fig. 1b. Pt(610) has 6 atoms in the terrace, Pt(410) has 4 atoms, and Pt(210) has 2 atoms. Hydrogen adsorption/desorption peaks are described in detail in the literature [25, 35]. It is shown [35] that the currents below 0.2 V are related to hydrogen adsorption/desorption on the steps of monoatomic height; the currents at 0.2–0.3 V correspond to terrace edges near the steps and those at 0.3–0.5 V are related to the central portion of the (100) terraces.

Currents of oxygen adsorption/desorption are observed in CVs at 0.8 V. They are maximal for narrow terraces, i.e., in this region of potentials, oxygen-containing particles (OCPs) are predominantly adsorbed on the steps and not on the terraces and can hinder adsorption of the other solution components. Prolonged conditioning in the oxygen region can distort the surface structure. However, brief conditioning in this region is not reflected on CVs and therefore on the electrode surface structure. Moreover, the electrode surface protected by copper adatoms is more stable towards oxidation.

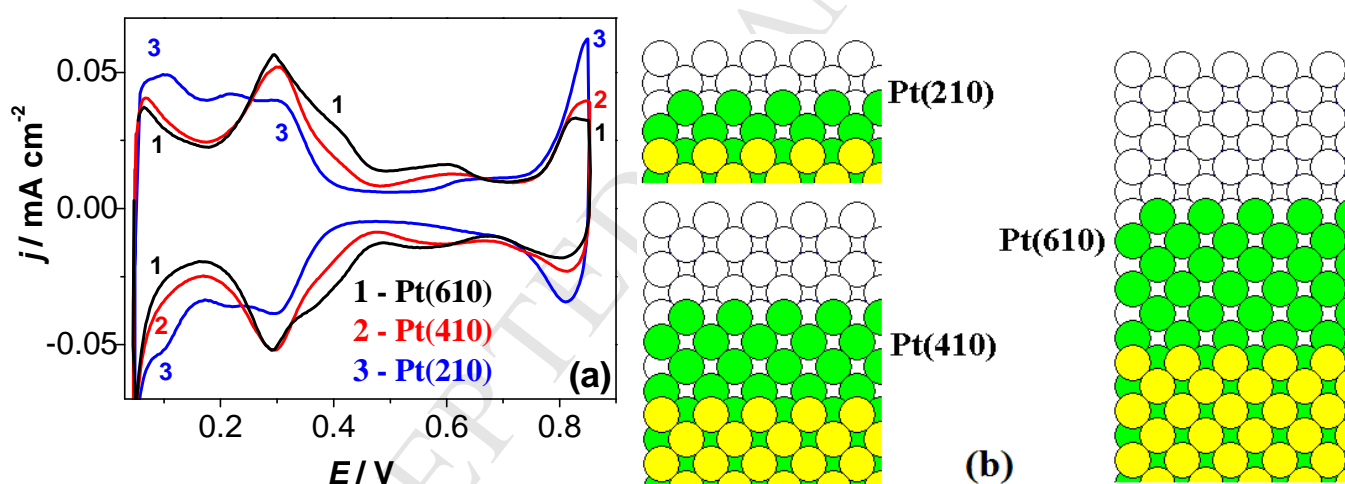


Fig. 1. (a) CVs of platinum single crystal electrodes in the 0.1 M HClO₄ solution: (1) Pt(610), (2) Pt(410), (3) Pt(210). The potential scan rate is 50 mV s⁻¹. (b) Schematic image of the structure of the corresponding stepped platinum single crystal faces.

Standard CVs in nitrate solution

Let us consider standard CVs on the above stepped single crystal electrodes in a nitrate solution (fig. 2a). As already mentioned above, the processes related to electroreduction of nitrate and its products and electrooxidation of these products on the Pt(100) terraces have already been studied in a series of prior works [20, 28-31]. Further, we assume that the characteristic peaks observed at similar potentials correspond to essentially the same species and the same products, as those determined in these works.

When the meniscus is formed at 850 mV and then the potential is shifted in the cathodic direction, nitrate is first reduced in the potential range of 850–400 mV to NO that partially blocks the surface. As the potential is shifted further in the negative direction, NO is reduced to NH_3 [29]. Nitrate electroreduction products are displaced from the surface by adsorbed hydrogen. At $E < 0.1$ V, the surface is mainly covered by hydrogen adatoms that prevent nitrate adsorption and its further reduction. When the potential sweep is reversed and potential is scanned from 50 mV up to 850 mV, hydrogen is desorbed first and then nitrate may adsorb on the free sites where it is reduced to NO, hydroxylamine and, possibly, ammonia. The currents in the sharp reduction peak at 330 mV depend on the terrace width: the wider it is, the more intensive the process. The same process continues up to 0.7 V, but the rate of ammonia formation at these potentials is smaller, the main product being NO [29]. At higher potentials (0.70–0.85 V), adsorbed hydroxylamine, or even ammonia, is oxidized to NO. The nature of the peak at 780 mV on Pt(100) is described in detail in [30]. One must point out that nitrate reduction currents on the narrow terraces of Pt(210), in the range of 300–500 mV of the negative-going scan, are the lowest, while the nitrate reduction peak at 200 mV is the highest in the studied electrode series: NO is slowly adsorbed on this surface and its intensive reduction starts only in the most negative potential region. In the positive-going scan, a slight current decrease is observed at 330 mV instead of the reduction peak. Also, there is no oxidation peak at 780 mV, because ammonia formed in the small amounts is desorbed from the electrode surface and does not participate in oxidation of ammonia to NO. The overall charge consumed in the reduction of nitrate is ca. $440 \mu\text{C}/\text{cm}^2$ on Pt(210), while in the case of Pt(410) it is ca. $460 \mu\text{C}/\text{cm}^2$ and it is ca. $530 \mu\text{C}/\text{cm}^2$ for Pt(610). Hence, though the nitrate reduction currents in the region of the reduction peak at 0.2 V are the highest on Pt(210), nitrate electroreduction occurs more actively on the wider (100) terraces, as shown by comparison of the overall charge consumed in electroreduction on nitrate on the different stepped surfaces.

One must point out that if the meniscus is formed at 50 mV and then the potential is shifted into the positive direction, then the voltammetric currents observed in the nitrate solution at the beginning of the first scan coincide with the currents in the pure supporting electrolyte, 0.1 M perchloric acid (curves 0 and 1 in fig. 2b), on all the electrodes. Hence,

nitrate (at the actual concentration of 20 mM NaNO_3 and at the sweep rate of 50 mV/s) cannot displace hydrogen from Pt(610), Pt(410), and Pt(210) up to 250 mV. The currents of the second and further cycles at 50 mV/s on Pt(610) and Pt(410) in the beginning of the hydrogen region, approximately up to 180 mV, are somewhat lower than in the first cycle (curve 2 in fig. 2b). Thus, some products of nitrate electroreduction partially block the steps. In the range of 180–250 mV, the voltammetric currents coincide in the nitrate solution and in the pure acid. At higher potentials, there is a small current decrease: though hydrogen adatoms partly desorb from the terrace edges and nitrate adsorption probably starts, the number of free sites is as yet insufficient for the intensive nitrate adsorption/reduction process that, as seen in the CV, starts at 300 mV. Let us point out that no such small reduction peak at 270 mV is observed on Pt(210). This can be explained by the fact that practically no hydrogen adatoms remain on the terrace after hydrogen desorption from the "terrace edge" (the terrace width is only 2 atoms) and nitrate adsorption and reduction are not possible.

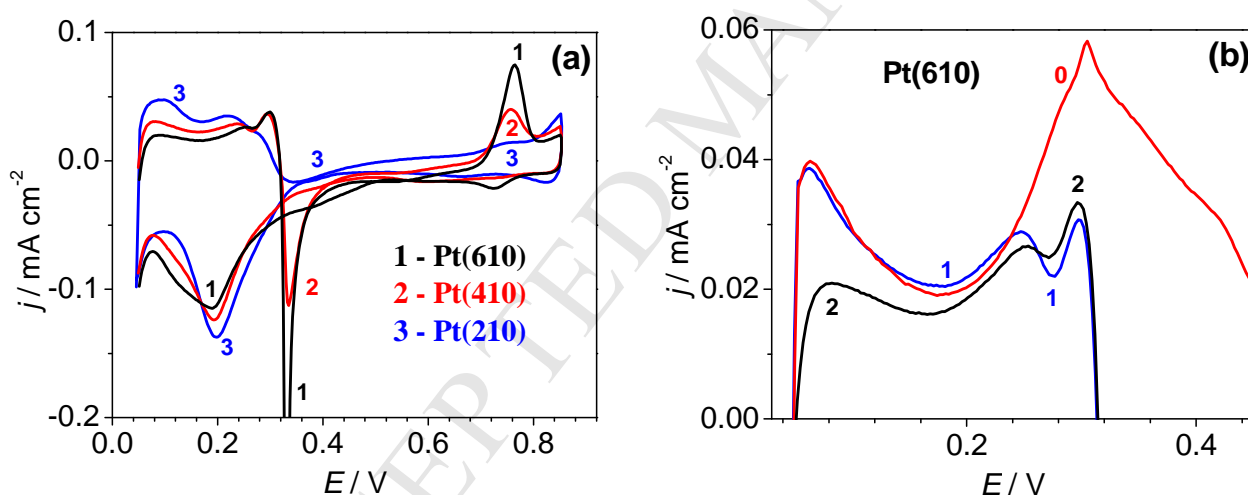


Fig. 2. (a) CVs of platinum single crystal electrodes in the solution of 0.1 M HClO_4 + 20 mM NaNO_3 : (1) Pt(610), (2) Pt(410), (3) Pt(210). (b) The initial section of CV of Pt(610): (0) the steady-state curve in 0.1 M HClO_4 , (1) the first scan after formation of the meniscus at 50 mV in the nitrate solution, (2) the second and the further scans in the nitrate solution. The potential scan rate is 50 mV s^{-1} .

Electrode modification by copper adatoms

As already pointed out above, surface properties can be changed by means of electrode composition modification by atoms of foreign metals. Let us first consider electrode modification in a nitrate-free copper solution.

The solution with a low copper concentration (10^{-5} M $\text{Cu}(\text{ClO}_4)_2$ and 0.1 M HClO_4) was used in order to prevent avalanching electrode surface filling by a copper monolayer

and to estimate the effect of the surface structure on the copper deposition process [20, 21].

Copper deposition was carried out under potentiodynamic control by electrode cycling in the copper adsorption region. The potentiodynamic mode proves to be more descriptive, as it allows constantly assessing the area of the electrode surface that is free of copper and available for hydrogen. The choice of the cycling limits is related to the fact that hydrogen currents drastically increase at the potentials below 50 mV, while the upper cycling limit must be more positive than the equilibrium copper deposition potential, but less positive than the potential of removal of the upd layer. Therefore, the upper limit chosen for the electrode modification was 350 mV. The surface coverage Cu_{ad} (Θ_{Cu}) can be estimated on the basis of the decrease in the currents in the hydrogen region or by integration of the copper desorption peak in the stripping region (see below in the next section and in fig. 6b). In these calculations, the monolayer charge is $414 \mu\text{C}/\text{cm}^2$ for Pt(610), $406 \mu\text{C}/\text{cm}^2$ for Pt(410), and $376 \mu\text{C}/\text{cm}^2$ for Pt(210), as follows from the packing density of the electrodes.

Fig. 3a shows a series of CVs (the numbers denote the number of accumulation cycles) of upd Cu deposition on Pt(610) in the range of 50–350 mV. One can see that deposition of adatoms occurs all over the electrode surface. As a result, peak currents drop in the whole range of hydrogen adsorption/desorption potentials, which means that copper is adsorbed both on the steps and on the terraces. However, during the first few deposition cycles, this process occurs more intensively on the steps and terrace edges, because in the first 5 cycles the currents decrease noticeably in the range of 50–150 mV and 220–320 mV that correspond to hydrogen adsorption/desorption on the steps and terrace edges, respectively (fig. 3a) [25, 35].

The anodic peak of upd copper dissolution from Pt(610) is split (fig. 3b), i.e., copper dissolution from steps and terraces can be clearly distinguished. Peak splitting is observed for surface coverages up to 0.4 ML. This surface coverage is characterized by the appearance of adatom islands (adatoms located on the neighboring adsorption sites) adjacent to the steps. Then the peak splitting disappears. As copper is accumulated on the surface, the peak of adatom desorption grows and shifts in the positive direction. The adlayer becomes ordered and stabilized (growth and coalescence of islands). After 100

accumulation cycles, the CVs still manifest a small hydrogen adsorption/desorption current. Here, free sites remain predominantly on terrace edges (the currents of desorption of hydrogen atoms at 270 mV). No peaks corresponding to copper phase dissolution can be seen in the CVs, whereas the peak of dissolution of copper adatoms shifts to the most positive potentials. At high electrode surface coverages by copper adatoms, the area of the anodic copper stripping peak almost stops growing and the currents in the range of 500–750 mV start increasing due to the beginning secondary decoration of steps (the second layer of copper adatoms covering the steps).

The surface of Pt(410) is covered by copper adatoms in a similar way. Fig. 3 shows the change in CVs in the course of accumulation (fig. 3c) and dissolution (fig. 3d) of copper adatoms. Dissolution of Cu_{ad} from the steps and terraces can be separated only at very small coverages. One can see clear separation of the peaks after two cycles of copper accumulation (0.12 ML), while there is only a single peak of copper dissolution after 10 cycles (0.27 ML). The decrease in the surface coverage by Cu_{ad} on Pt(410), at which the peak splitting disappears, as compared to Pt(610), is quite consistent, because the terrace width decreases.

A somewhat different pattern is observed in the case of formation of the adatom monolayer on Pt(210) (figs. 3e,f). There is no splitting of the stripping peak related to separate step and terrace contributions at any coverage and there is no shift of this oxidation peak at the increasing surface coverage (very narrow steps). However, the currents of secondary decoration start growing already at 30 copper accumulation cycles.

One must point out that at potentials to the negative of the equilibrium value copper crystallites can be formed on adatom islands at large surface coverages by copper adatoms. However, these particles are dissolved in every cycle at potentials more positive than the equilibrium value, thus making no noticeable contribution to the true electrode surface area. The probability of formation of such particles grows at a decrease in the terrace width, as the steps are active sites for the copper nucleation process. A small peak corresponding to copper phase dissolution is observed in CVs only for Pt(210) after 50 accumulation cycles. The mechanism of upd Cu formation on stepped surfaces with (100) terraces and (110) steps on Pt(610) and Pt(410) is described in more detail in [27].

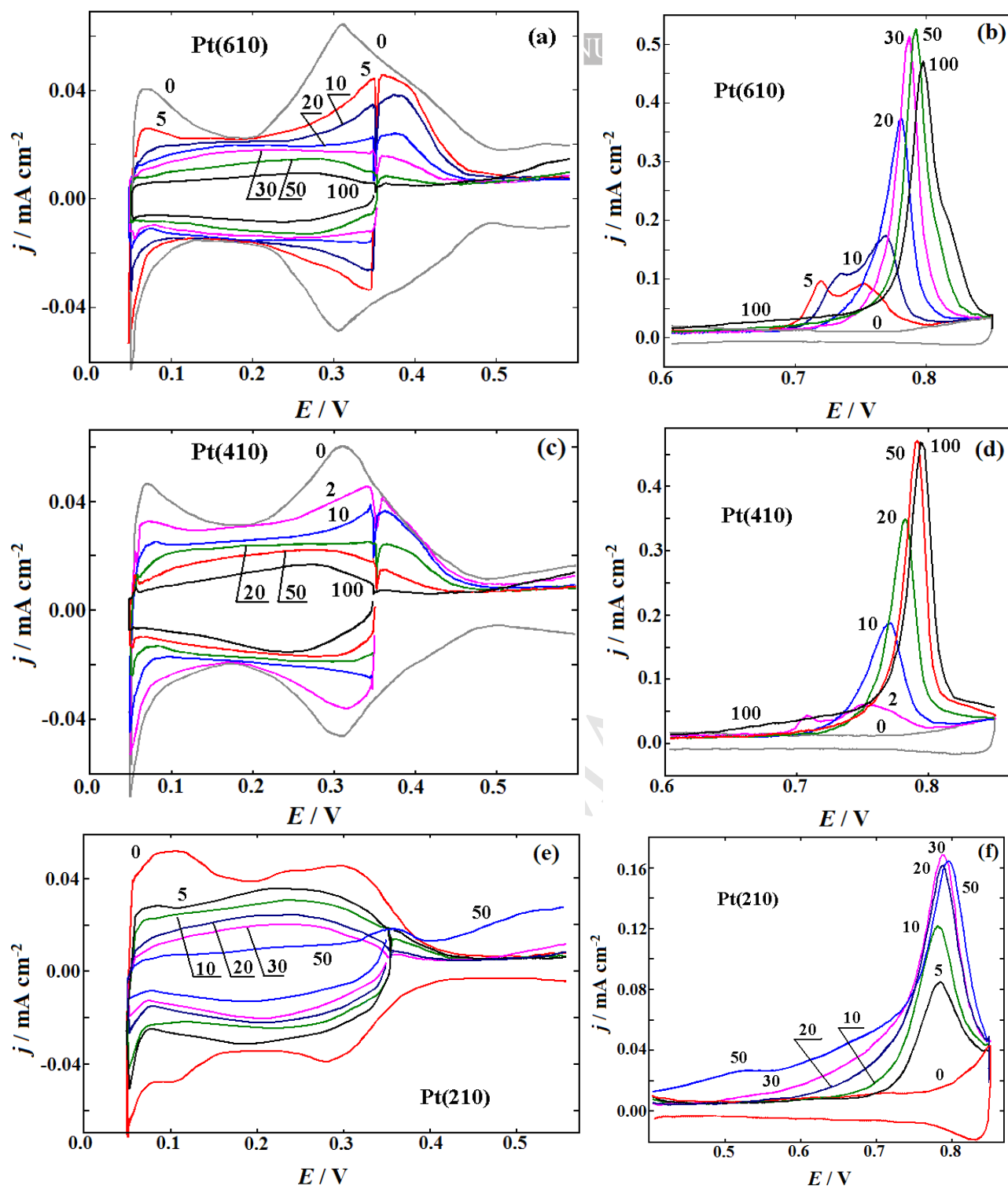


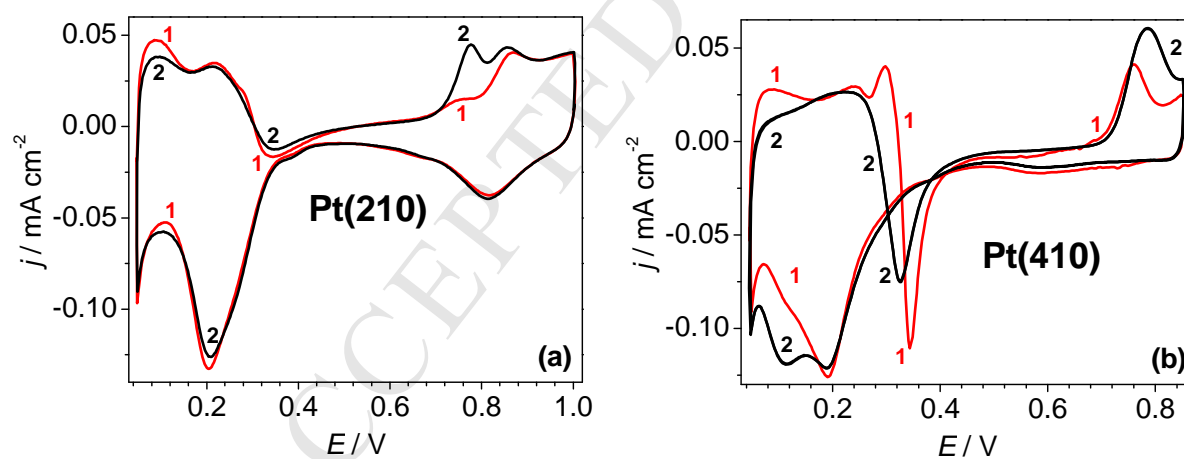
Fig. 3. CVs of copper accumulation (a, c, e) and dissolution (b, d, f) in the solution of 0.1 M $\text{HClO}_4 + 10^{-5}$ M $\text{Cu}(\text{ClO}_4)_2$ on Pt(610) (a,b), Pt(410) (c, d) and Pt(210) (e, f). The potential scan rate is 50 mV s^{-1} .

Nitrate electroreduction on copper-modified electrodes

There is a number of difficulties related to the transfer of a formed full (or partial) up layer from a copper solution to a cell with a nitrate solution for studying nitrate electroreduction under controlled conditions. On the one hand, the copper adlayer is well preserved during the transfer if it has been formed in a sulfuric acid solution, as sulfate anions are adsorbed on copper and protect it from dissolution. However, traces of sulfate

complicate nitrate reduction. On the other hand, if the monolayer has been formed in a copper solution in perchloric acid, then the major part of the adlayer can be lost in the course of the electrode transfer to a different cell. Thus, it may be practical to modify the electrode by copper adatoms directly in the nitrate-containing perchloric acid solution.

Let us first consider steady-state curves of nitrate electroreduction in the copper solution (fig. 4). As we showed earlier, there is no peak at 780 mV on Pt(100) in the presence of the complete copper adlayer [20]. However, the contribution of this peak to the copper stripping on stepped electrodes cannot be neglected, especially at small copper surface coverages. While this contribution can be ignored on Pt(210) (fig. 4a), it is impossible to estimate the charge contribution due to copper desorption under this peak for Pt(410) and Pt(610) (fig. 4b,c), as both processes occur in the same potential range. Moreover, the copper desorption peak on Pt(610) is shifted in the positive direction already after 5 copper accumulation cycles and the peak of the ammonia-NO transition disappears completely (fig. 4d). This is not similar for Pt(410), but the contribution of the ammonia-NO transition currents into the copper desorption currents is negligible for this electrode, as the area of this peak is small in a copper-free nitrate solution and this contribution must be even lower on a surface partly covered by copper (fig. 4e).



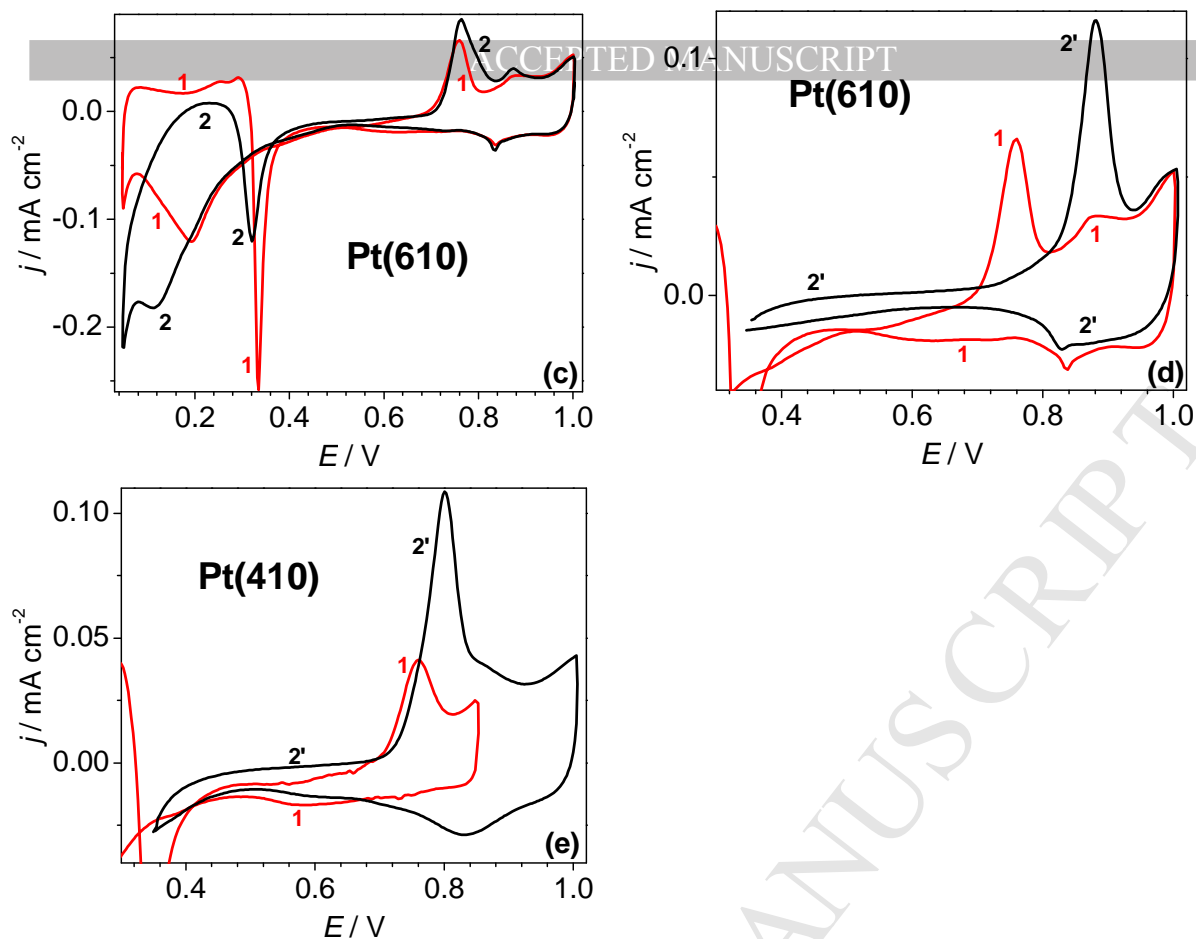


Fig. 4. Steady-state CVs in the solution of (1) 0.1 M HClO₄ + 20 mM NaNO₃, (2) 0.1 M HClO₄ + 20 mM NaNO₃ + 10⁻⁵ M Cu(ClO₄)₂, (2') after 5 copper accumulation cycles in the solution of 0.1 M HClO₄ + 20 mM NaNO₃ + 10⁻⁵ M Cu(ClO₄)₂ on (a) Pt(210), (b, e) Pt(410), (c, d) Pt(610). The potential scan rate is 50 mV s⁻¹.

Let us now consider the process of nitrate electroreduction during the simultaneous copper codeposition from the solution. When copper ions are added to the solution, even at a low concentration, the rate of nitrate electroreduction on the (100) terraces starts growing, as compared to pure nitrate solution as a result of copper accumulation on the electrode. For Pt(210), there is a certain "incubation period" for the growth of nitrate reduction currents due to the slow removal of oxygen-containing particles from the steps. Fig. 5 shows voltammograms of nitrate reduction during copper deposition from the solution of 0.1 M HClO₄ + 20 mM NaNO₃ + 10⁻⁵ M Cu(ClO₄)₂ in the range of 50–350 mV on the different electrodes. The numbers near the curves correspond to cycle numbers. A characteristic feature of the Pt(210) electrode (fig. 5a) is that the currents in the first cycle are close to the currents in the hydrogen region of the corresponding CV in a copper-free solution (curve 3 in fig. 2). Calculation of the difference between hydrogen desorption

charges in the nitrate solution and in the copper-containing nitrate solution shows that there is approximately 0.026 ML of copper on the surface after the first cycle in the range of 350–50 mV. In the second cycle, nitrate reduction currents in the negative-going scan are much lower than in the first cycle: though a part of adsorption sites is already occupied by copper adatoms, but their amount is still insufficient for observing any significant decrease in the local surface charge density (copper has a partial positive charge [22, 36]) to induce adsorption of nitrate anions. Another reason for the current decrease in the second cycle as compared to the first one is related to the history of the cycling: the first cycle occurs after the electrode conditioning in the range of potentials, where NO is adsorbed on the surface (formation of the meniscus at 850 mV). Let us point out that copper is first predominantly deposited on the steps; this is confirmed by the decrease in the currents of hydrogen desorption from cycle to cycle in the potential range of 50–180 mV in the beginning of the anodic scan.

In the course of cycling, the currents in the cathodic scan on Pt(210) slowly decrease in the range of 350–180 mV (nitrate electroreduction on platinum) and slowly increase in the range of potentials of 180–50 mV. Here, nitrate reduction occurs not only on platinum, but also on the copper-covered surface, while adsorption of hydrogen adatoms only occurs on copper-free sites after desorption of products of the nitrate reduction reaction.

The process of nitrate electroreduction on Pt(410) is more active (fig. 5b). Nitrate reduction currents in the cathodic scan increase noticeably with each cycle. The currents of nitrate reduction to NH_3 at 330 mV in the anodic scan gradually decrease as copper is accumulated on the surface. This process corresponds to a sharp peak only on the unmodified platinum surface after partial desorption of hydrogen from the terraces and in this case nitrate reduction continues all over the positive scan.

On Pt(610), the electroreduction process occurs even more intensively (fig. 5c). The currents of nitrate reduction to NH_3 at 330 mV are observed only in the first scan and they are already several times lower than on unmodified platinum.

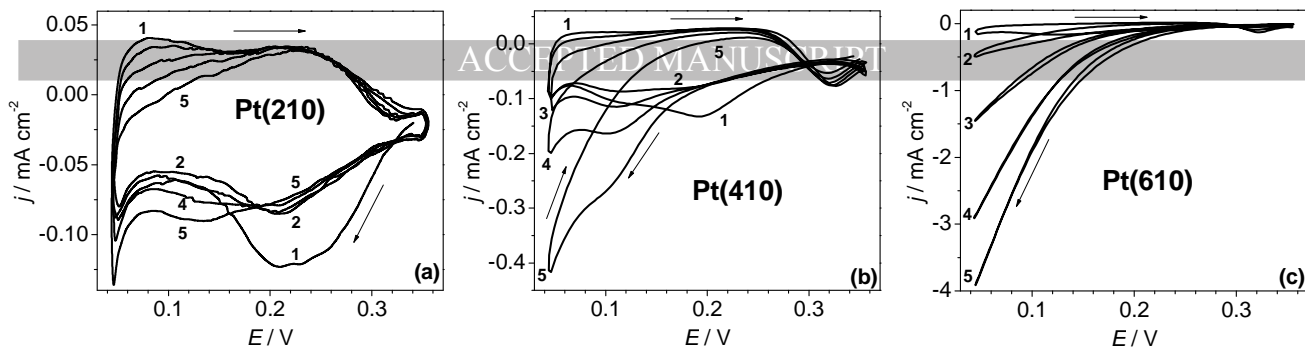


Fig. 5. CVs of five successive cycles in the potential range of 50–350 mV in the solution of 0.1 M HClO_4 + 20 mM NaNO_3 + 10^{-4} M $\text{Cu}(\text{ClO}_4)_2$ on (a) Pt(210), (b) Pt(410), (c) Pt(610). The numbers denote cycle numbers, the arrows indicate the direction of the potential sweep. The potential scan rate is 50 mV s^{-1} .

Fig. 6a compares the nitrate reduction currents in the fifth copper deposition cycles on the different electrodes. While the nitrate reduction currents in the negative sweep increase in the range of potentials around 200 mV in a copper-free nitrate solution in the sequence of $\text{Pt}(610) < \text{Pt}(410) < \text{Pt}(210)$ (fig. 2a), this dependence is reversed in the copper-containing nitrate solution: the wider the terraces, the higher the currents. Fig. 6b shows CVs of copper dissolution in the range of 350–1000 mV. All electrodes manifest sharp, well defined peaks. There is a slight positive shift in the copper dissolution potential. To estimate the amount of copper on the surface, the peak of copper dissolution was integrated from the potential at which the current in the CV passed through zero, to the beginning of the oxygen region for Pt(210) and to the beginning of the NO–nitrite transition for Pt(410) and Pt(610) [30, 31], with correction for the background curve. Here, the background curve was assumed to be the second cycle in the same range of potentials (see, e.g., the inset in fig. 6b). The higher the current of nitrate reduction, the larger the error in such calculations, because cathodic currents of nitrate reduction are superimposed on the initial section of the anodic scan. However, this procedure allows estimating the amount of copper adatoms on the surface. Five cycles resulted in accumulation of approximately 0.20–0.25 monolayers (ML) of copper. These values are very similar for the different electrodes used. Such coverages most probably correspond to the simultaneous presence of individual copper adatoms and small islands of copper adatoms on the surface. Thus, the difference in the nitrate reduction currents cannot be explained by just the amount of copper on the surface, because these amounts are almost similar.

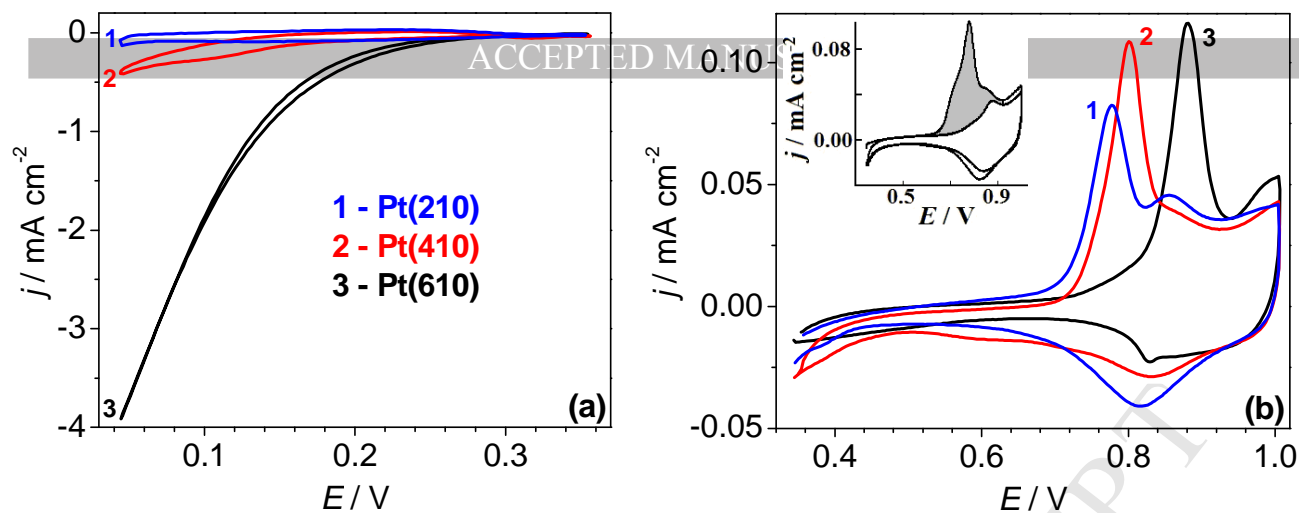


Fig. 6. (a) CVs of the fifth nitrate electroreduction cycle in the potential range of 50–350 mV simultaneously with copper accumulation. (b) CVs of copper dissolution after 5 deposition cycles. (1) Pt(210), (2) Pt(410), (3) Pt(610). The inset (Pt(210), 20 accumulation cycles) shows the integration region for charge estimation. The solution is 0.1 M HClO₄ + 20 mM NaNO₃ + 10⁻⁵ M Cu(ClO₄)₂. The potential scan rate is 50 mV s⁻¹.

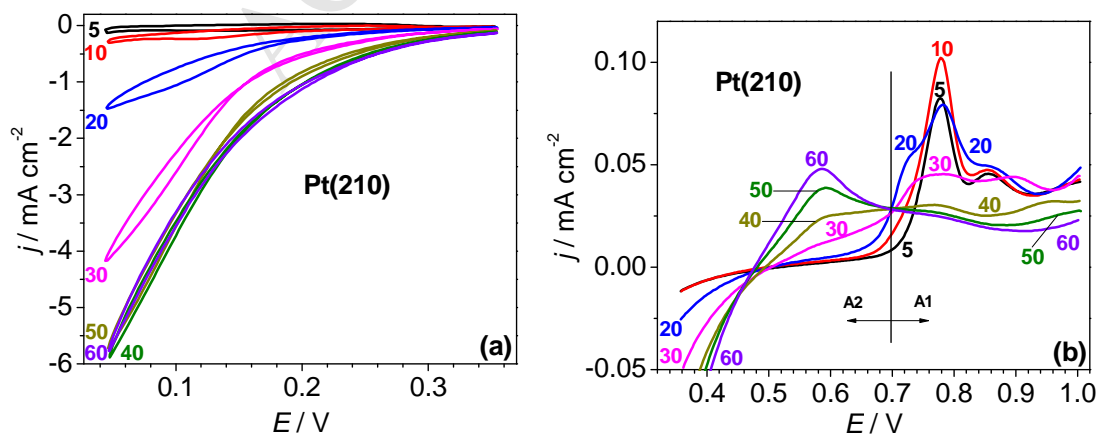
It should be pointed out that in our case the values of the reduction currents in the meniscus configuration depend on the electrode diameter and meniscus height (supply and removal of products of the nitrate reduction reaction). This may also affect the comparison of different electrodes (though the difference in the current values is too high to consider the effect of this transport-related problem significant), especially in the case of prolonged copper accumulation, as nitrate electroreduction occurs very intensively. Moreover, the same characteristic changes are observed for all the electrodes in different experiments.

Let us consider now the evolution of CVs of up Cu dissolution from the electrode surface after deposition with simultaneous electroreduction of nitrate anions. As can be seen from the curves in fig. 7, a pronounced sharp peak (A1) is observed at first in CVs of Pt(610) and Pt(410) after 5 cycles of copper accumulation. This peak apparently corresponds mainly to dissolution of individual copper adatoms. Copper atoms are preferably adsorbed apart from each other, both on the steps and terraces, as they possess partial positive charge [22, 36]. As follows from the surface geometry, this possibility remains until the surface coverage reaches approximately 0.3 ML, after which island formation becomes unavoidable. As the number of accumulation cycles increases, the stripping peak charge grows and the peak potential is shifted in the positive direction. This reflects the ordering of the structure of the copper adlayer, as adatom islands, i.e., groups of adatoms occupying neighboring sites, are formed on the surface. Then the charge of

this peak decreases and stabilizes and yet another copper desorption peak (A2) appears in the potential range of 0.6–0.7 V. For Pt(610), peak A1 is still observed even after prolonged copper accumulation, while for Pt(410) it practically disappears after 40 accumulation cycles.

As copper is accumulated, the current in peak A1 in the case of Pt(210) (fig. 7b) first increases without any peak potential shift and then the peak broadens (different energy states of the desorbing copper) and practically disappears for 40–60 cycles. In other words, all electrodes manifest a decrease in the charge of peak A1 and an increase in peak A2 starting from a certain copper surface coverage.

This can hardly be related to changes in the electrode surface; prolonged copper accumulation was always followed by an experiment with just a few cycles of copper accumulation, in which the sharp A1 peak remained in the potential window characteristic for the corresponding electrode. We relate these changes to adlayer redistribution in the course of copper accumulation under the conditions of intensive nitrate reduction. Besides, the adsorption layer can be chemically etched in this range of potentials in the presence of nitrate in the solution. In the case of a large number of accumulation cycles, small copper islands can be partially dissolved from the terraces due to chemical etching, while larger islands are preserved. However, the adatoms cannot be reincorporated into the already existing islands due to the competing adsorption of nitrate and its reduction products. As copper is more strongly adsorbed in the steps, the newly adsorbed atom fills the position of "secondary decoration" when the terrace sites are no more available. In this case, the main dissolution peak A1 should decrease and broaden. At the same time, currents corresponding to dissolution of less stable adatoms (peak A2) will appear in the range of lower potentials.



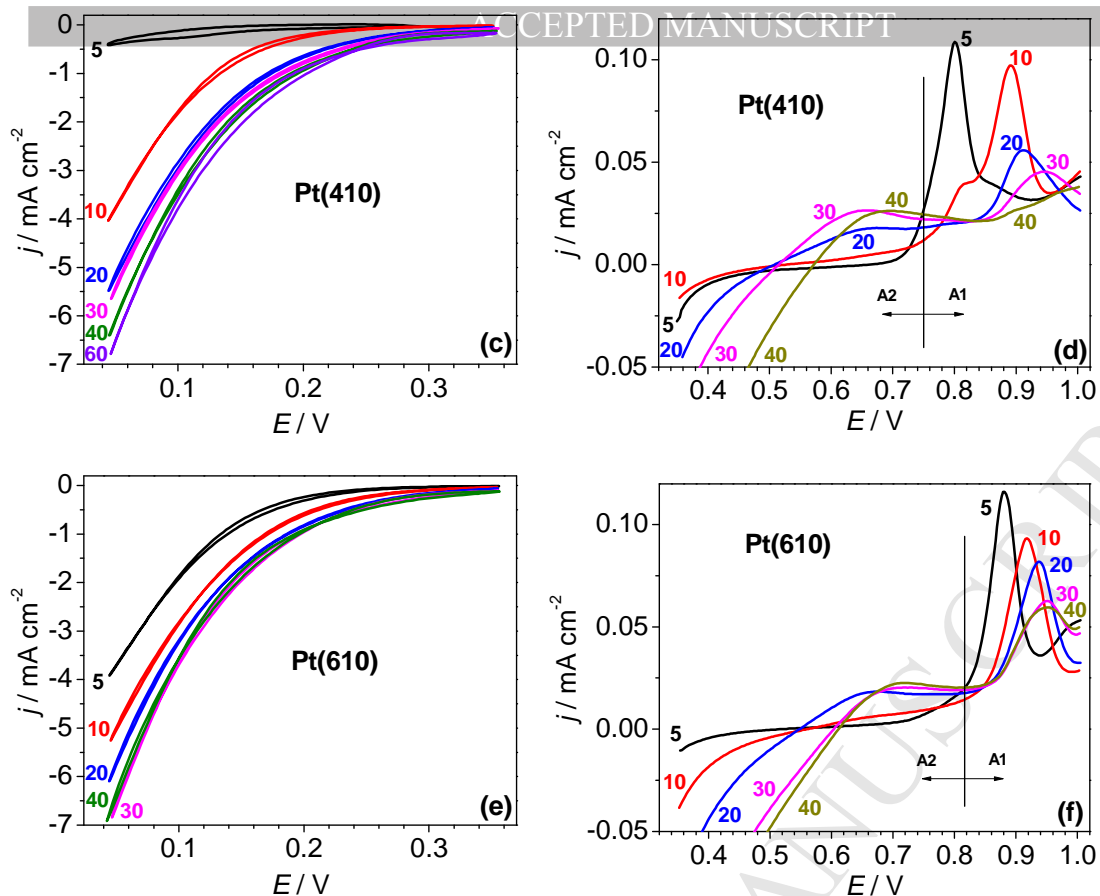


Fig. 7. CVs of nitrate reduction in the course of accumulation (a, c, e) and dissolution (b, d, f) of copper adatoms after different numbers of copper accumulation cycles (numbers near the curves) in the range of 50–350 mV in the solution of 0.1 M HClO_4 + 20 mM NaNO_3 + 10^{-5} M $\text{Cu}(\text{ClO}_4)_2$ on (a, b) Pt(210), (c, d) Pt(410), (e, f) Pt(610). The potential scan rate is 50 mV s^{-1} .

Here, nitrate reduction currents grow on all the electrodes and gradually reach a certain limiting value (see figs. 7a, c, e). They can even slightly decrease, which we associate with depletion of the nearelectrode layer by copper or by nitrate. The wider the terraces, the faster the increase in the nitrate reduction currents.

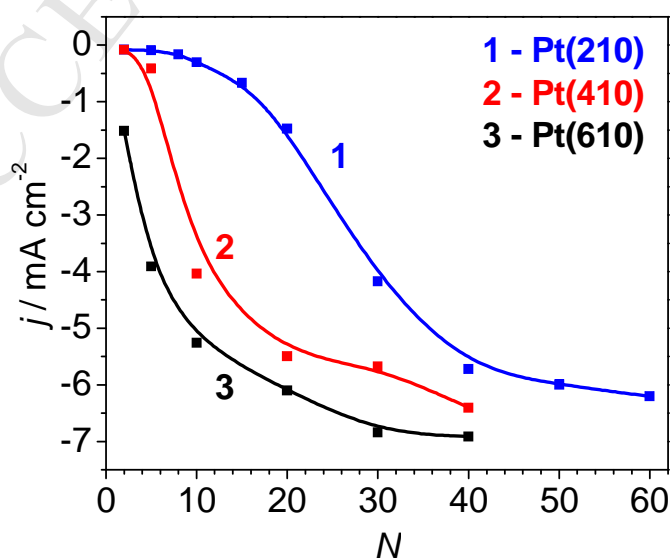


Fig. 8. Dependence of the nitrate reduction current at 50 mV on the number of copper accumulation cycles in the solution of 0.1 M HClO₄ + 20 mM NaNO₃ + 10⁻⁵ M Cu(ClO₄)₂ on (1) Pt(210), (2) Pt(410), (3) Pt(610).

Fig. 8 shows the dependence of the nitrate reduction current at 50 mV on the number of copper accumulation cycles for different electrodes.

One should take into account that there is more, and not less, copper on narrow terraces of the Pt(210) electrode, as compared to Pt(610). For 20 cycles, $\Theta_{\text{Cu}} = 0.56$ ML for Pt(210) and $\Theta_{\text{Cu}} = 0.40$ ML for Pt(610), while the nitrate reduction currents at 50 mV in the latter case are four times higher. Therefore, the presence of copper on the surface is by itself an insufficient condition for the high rate of nitrate reduction. The difference in the rates decreases at an increase on the number of accumulation cycles. At the same time, the greater the number of cycles, the higher the error in estimation of Θ_{Cu} , as copper desorption currents are superimposed on nitrate reduction making impossible the correct evaluation of Θ_{Cu} at large numbers of accumulation cycles.

The greatest change both in the rate of nitrate electroreduction and the copper adlayer structure as dependent on the number of copper accumulation cycles is observed for Pt(210) in figs. 8 and 7b. For five copper accumulation cycles, the currents of nitrate reduction are very low, even lower than in the copper-free solution. Individual copper adatoms and small copper islands cannot cause a sufficient decrease in the local surface charge that would provide enhanced nitrate adsorption on narrow terraces. The curve of copper desorption still manifests a pronounced separate peak even after 20 accumulation cycles, fig. 7b. However, no stable layer is formed on the platinum surface with narrow terraces, as peak A1 is not shifted into the anodic direction and keeps broadening. After 20 cycles of copper accumulation, the currents of nitrate reduction grow drastically, simultaneously with the attainment of the maximum amount of copper on the surface and, therefore, the greatest decrease in the surface charge. The further increase in the number of accumulation cycles results in a profound change in the structure of the copper adsorption layer and peak A1 practically disappears. Thus, one may conclude that intensive reduction of nitrate on the surface of single crystal electrodes requires the presence of individual Cu adatoms and/or adatom islands on the terraces that promote adsorption of the nitrate anion. Hence, a certain fraction of platinum sites must remain free. Such situation is more easily achieved on the wider terraces of Pt(610). The Pt(410)

electrode occupies the intermediate position between Pt(210) and Pt(610), both in relation to copper coverage and nitrate reduction currents. In the case of Pt(610), an inflection appears at the beginning of the anodic copper desorption scan after 40 accumulation cycles, which can be attributed to dissolution of a small amount of the copper phase. No such inflections are observed on Pt(410) and Pt(210). To avoid the effect of accumulation of nitrate reduction products in the nearelectrode layer and diffusion limitations by copper on nitrate reduction, it is thus advisable to compare just the first 20–30 copper accumulation cycles on different electrodes.

Another interesting fact observed during nitrate reduction in the presence of copper is the shift in the copper desorption potential with respect to the peak in the nitrate-free solution. Fig. 9 compares the copper dissolution peaks in the range of 50–350 mV in perchloric acid containing 10^{-5} M $\text{Cu}(\text{ClO}_4)_2$ (curve 1) and in the perchloric acid solution containing both nitrate and 10^{-5} M $\text{Cu}(\text{ClO}_4)_2$ (curve 2) on Pt(210), Pt(410), Pt(610). The potential of the peak of the Cu_{ad} monolayer stripping in the nitrate-free perchloric acid solution depends more on the perfection of the adlayer than on the terrace width. The partial adlayer (except for that on Pt(210)) starts dissolving earlier than the full adlayer: the potential of the copper dissolution peak shifts in the positive direction at an increase in Θ_{Cu} . Usually, the copper monolayer is completely removed from the surface at 50 mV s^{-1} by 850 mV. However, in the case of a solution also containing 20 mM NaNO_3 , Cu_{ad} is dissolved at more positive potentials (figs. 9b,c). One can see that the peak shift grows with the increasing terrace width (compare figs. 9a,b,c). At the same time, on Pt(210), where the terraces are narrow, anodic copper dissolution peaks both in the nitrate-free solution and in the nitrate-containing solution are observed at practically the same potential. This effect can be explained as follows. Presumably, NO stabilizes copper adatoms in this range of potentials, when it is adsorbed on platinum terraces along the perimeter of copper islands and prevents the breakaway of the edge atoms from the copper islands. In the case of narrow terraces coadsorption of copper and NO is complicated, which interferes with such stabilization.

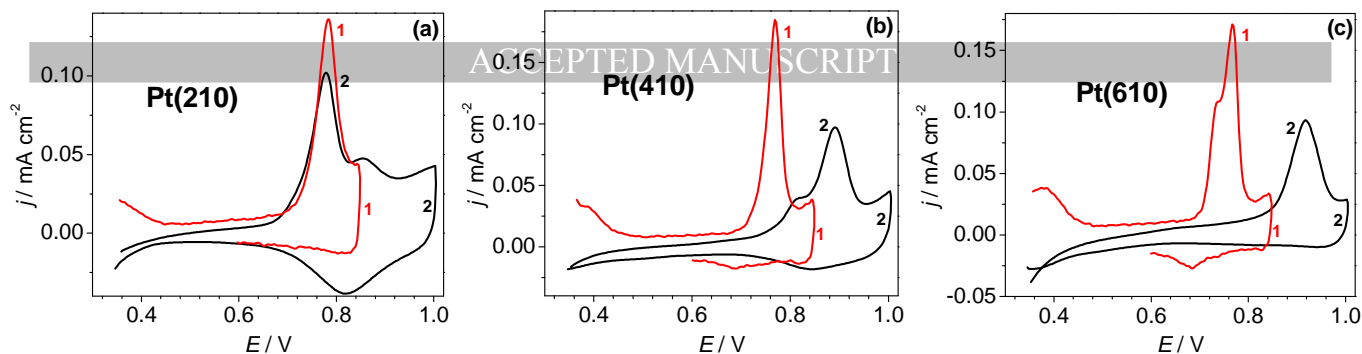


Fig. 9. Anodic CV scans of copper dissolution after 10 accumulation cycles on (a) Pt(210), (b) Pt(410), (c) Pt(610). (1) 0.1 M HClO_4 + 10^{-5} M $\text{Cu}(\text{ClO}_4)_2$, (2) 0.1 M HClO_4 + 20 mM NaNO_3 + 10^{-5} M $\text{Cu}(\text{ClO}_4)_2$. The potential scan rate is 50 mV s^{-1} .

CONCLUSIONS

Correlation of the nitrate reduction currents with the corresponding copper dissolution currents allows assuming that:

Copper is adsorbed on Pt(210) on the steps and there is practically no space for strong adsorption of the flat nitrate anion. For 2–10 copper accumulation cycles, the currents of nitrate reduction are very low. At an increase in the copper amount on the surface, the surface charge decreases and more nitrate anions are discharged, i.e., the current of nitrate reduction increases.

On Pt(410), individual copper atoms are at first adsorbed predominantly on the steps; meanwhile, the terraces are occupied by nitrate and NO. The currents of nitrate reduction for 2–5 copper accumulation cycles are low. A separate dissolution peak is observed at 800 mV with a small shoulder at 850 mV. When considerable amounts of copper are adsorbed on the terraces, the current of nitrate reduction drastically increases.

On Pt(610), the current reaches about 1.5 mA/cm^2 already after two cycles in the range of 50–350 mV; the amount of copper on the surface in this case cannot be estimated quite correctly. For 5 cycles, $\Theta_{\text{Cu}}=0.22 \text{ ML}$, i.e., copper adatoms or islands are present not only on the steps, but also on the terraces. The currents in this case are almost an order of magnitude higher than those on Pt(410).

Hence, one can conclude that:

1. In perchloric acid solution on stepped single crystal electrodes modified by copper adatoms, the rate of nitrate reduction increases by up to two orders of magnitude, as copper is accumulated on the surface as a result of potential cycling in the range of 50–350 mV. At low copper surface coverages, there is a pronounced dependence of the nitrate

reduction rate on the terrace width. The rate grows in the sequence of Pt(210) < Pt(410) < Pt(610).

2. At an increase in the duration of nitrate reduction with simultaneous copper deposition, the rate of nitrate reduction continues growing in the sequence of Pt(210) < Pt(410) < Pt(610), but the difference in the reduction rates on different electrodes decreases. A change in the reaction products is possible in case of prolonged nitrate reduction on modified electrodes.

3. The peak of dissolution of copper adatoms in the nitrate solution is shifted in the anodic direction as compared to the nitrate-free solution due to stabilization of copper adatoms by adsorbed NO. The extent of the shift depends on the terrace width: the wider the terraces, the larger the peak shift. This is probably related to formation of ordered islands of coadsorbed NO and copper. No such shift is observed for Pt(210) with a terrace width of only 2 atoms.

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- Pt(S)-[n(100)x(110)] electrodes are modified by Cu adatoms with different coverages
- Nitrate reduction is strongly promoted on Cu-modified Pt electrodes
- Nitrate reduction is the faster on Pt/Cu_{ad}, the wider the (100) terraces
- The Cu desorption peak in nitrate solutions is shifted in the anodic direction
- Prolonged nitrate reduction with Cu accumulation causes Cu adlayer restructuring

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