New Insights into the Redox Behavior of Adsorbed NO on Pt(111) and Vicinal Surfaces Containing Monoatomic (111) and (100) Steps

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The process of nitrate electroreduction is attractive to researchers due to scientific (study of a multistage reaction, interest towards intermediates) and practical (water treatment) aspects. NO is one of the key intermediates in nitrate electroreduction [1]. The electrochemical behaviour of NO on platinum electrodes represents an important part of the electrochemistry of nitrogen-containing compounds. The use of single crystal Pt electrodes with well-defined surfaces of different orientation allows establishing correlations between the structure of adsorption sites and their reactivity towards NO electroreduction that is characterized by strong adsorption on electrode surfaces. Previously, redox transformations of preadsorbed saturated NO layers were studied on different Pt(hkl) electrodes [1-4]. Fig. 1a,b shows typical cyclic voltammograms of Pt(111) covered with a saturated NO adlayer. The potential sweep in the negative direction down to 0.05 V leads to reduction of the whole NO adlayer to NH_{4^+} [1]. NH_{4^+} is displaced by hydrogen adsorption, and the successive voltametric cycle is nearly identical to that recorded on a clean Pt(111) electrode in the absence of NO. The potential sweep in the positive direction up to 1.10 V leads to oxidation of NO_{ads} to (NO₂⁻)_{ads} (Fig. 1b). As opposed to complete NO adlayer stripping, partial reduction of compact NO adlayers was studied in sufficient detail only for Pt(100) surfaces, but is as yet not described for the (111) plane. Partial reduction of NO_{ads} occurs in the course of a slow potential sweep to $E_{cat} > 0.05$ V (Fig. 1c). The further CVs recorded in the range, where no further NO_{ads} reduction occurs, display a new pair of stable redox peaks at ~0.6 V. These peaks are attributed to redox transformations between NH_4^+ (or $NH_{3,ads}$) and intermediate ($N_xO_yH_z$)_{ads} species. The nature of $N_xO_yH_z$ on Pt(111) is under debate, though in the case of Pt(100) it was attributed to NO_{ads} [4]. The pair of peaks at 0.72 V appears after reduction of a yet larger fraction of NO_{ads} and is attributed to adsorption/desorption of OHspecies. Additional experiments are performed on stepped Pt(hkl) electrodes with (111) terraces and (111) or (100) steps. The increase in the concentration of the steps leads to a decrease in the intensity of the $NH_{3,ads} \leftrightarrow (N_xO_yH_z)_{ads}$ redox process, indicating that this process occurs on the (111) terraces. The nature of steps also plays a role in $NH_{3,ads} \leftrightarrow (N_xO_yH_z)_{ads}$ transformations: the intensity of this process is higher on stepped Pt electrodes with (100) steps. In our presentation we will attempt to elucidate the origin of this redox process.



Fig. 1. CVs of Pt(111) electrode covered with a monolayer of NO in 0.1 M HClO₄. The scan rate was 50 mVs⁻¹ (solid lines) and 5 mVs⁻¹ (dashed lines). (a) Reductive stripping of a compact NO monolayer. (b) CV in a positive potential range showing reversible oxidation of NO. (c) Reduction of a part of NO adlayer by potential sweep (5 mVs⁻¹) to E_{cat} (0.30 and 0.15 V) followed by CV started in the positive direction at 50 mVs⁻¹.

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