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NO_x-induced deactivation of Pt electrocatalysis towards the ammonia oxidation reaction

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ABSTRACT

An understanding of the deactivation mechanism of Pt electrocatalysis towards the ammonia oxidation reaction (AOR) to dinitrogen is key to the successful introduction of the nitrogen energy cycle, which can be used as a source of hydrogen fuels. Herein, we study AOR electrocatalysis on NO_x-adsorbed polycrystalline Pt electrodes, i.e. NO, NO_2^- and NO_3^-, and find that all the NO_x species can significantly reduce the catalytic activity of Pt. Combined stationary/transient voltammograms reveal that the poisonous NO_x species are produced by NH_3 oxidation on the bare Pt surface, but the adsorbed NO_x species can be transformed to N_2 by the Langmuir–Hinshelwood mechanism with *NO as a key intermediate.

1. Introduction

The electrochemical oxidation of ammonia to dinitrogen, i.e. the reverse Haber–Bosch process, has received much attention because of its important applications in sensors and decontamination [1]. Meanwhile, the ease of liquefaction (e.g. 10 bar at room temperature) and high hydrogen content (i.e. 17.7 wt%) of NH_3 indicate its potential utility as a carbon-free energy carrier, primarily for electrolytic H_2 production and electricity generation from fuel cells [1,2].

Platinum is one of the best AOR catalysts, with dehydrogenation of NH_3 and consecutive N—N coupling reactions occurring on its surface [3–5]. However, poisoning agents generated on the Pt surface significantly reduce its initial catalytic activity. In the Gerischer–Mauerer mechanism, N—N bond formation occurs through recombination of two $^*NH_x$ species ($x = 1$ or 2, asterisk indicating an adsorbed species) [6], while fully dehydrogenated *N is a poisoning agent hindering N_2 formation. However, the fast deactivation of AOR catalysis on Pt may be more complicated. Despite the relatively low thermodynamic potential of AOR (0.055 V vs. reversible hydrogen electrode (RHE)), its sluggish kinetics practically require an operating potential of $> 0.6\ V_{RHE}$, which may induce formation of byproducts such as oxygenated nitrogen species once the catalyst surface is oxidized [7–10]. While oxygenated nitrogen species are not considered in the traditional AOR mechanism (or in the Oswin–Salomon mechanism which suggests N—N coupling involving two *N species [11]), recent studies have observed the formation of such species with advanced spectroscopic methods, e.g. differential electrochemical mass spectroscopy (DEMS) and in situ infrared spectroscopy [12–19]. The potential influence of oxygenated nitrogen intermediates or products on the AOR mechanism should therefore be considered, in particular as site-blocking agents and/or inhibitors of N—N bond formation.

In the present study, polycrystalline Pt surfaces are chemically treated with three representative oxygenated nitrogen species (NO, NO_2^- and NO_3^-), and their AOR behaviors are compared with those of bare Pt. We found that all $^*NO_x$ species are strongly bound to the Pt surface and impede efficient N_2 formation, but their removal via N—N coupling with $^*NH_x$ to N_2 (i.e. the Langmuir–Hinshelwood mechanism) may be possible with *NO as a key intermediate.

2. Experimental

Electrochemical analyses were performed with a VMP3 potentiostat (Bio-Logic Science Instruments) in a beaker cell equipped with a graphite rod counter and Ag/AgCl reference (RE-16 for strong alkaline media, polyether ether ketone body (PEEK), EC-Frontier) electrodes. To avoid glassware dissolution and halogen poisoning [20,21], the cell was made of Teflon, and the reference electrode was doubly separated with a PEEK bridge tube. A 3-mm-diameter polycrystalline Pt electrode (PT-6355, EC-Frontier) was used as the working electrode after mirror polishing with alumina slurry (0.05 μm, R&B Inc.).

Ar-saturated 0.1 M KOH solution with or without 1 mM NH_3, which was prepared with ultrapure water (> 18.2 MΩ, Arium® mini, Sartorius), KOH (99.99% trace metals basis, Sigma-Aldrich) and concentrated NH_3 solution (25 wt%, Merck), was used as an electrolyte.

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The reference electrode was calibrated against a Pt electrode in the H_2-saturated electrolyte, and all potentials were reported on the RHE scale. The Pt electrode was first cleaned by running 50 CV cycles in the potential range 0.05–1.2 V_{RHE} at a scan rate of 200 $mV\,s^{-1}$. Afterwards, NO_x species were adsorbed by dipping the Pt electrode in NO-saturated (C_{NO} = ca. 2 mM) or 2 mM NO_2^-/NO_3^--dissolved 0.1 M KOH solution, which was prepared with NO gas (3 N, Daedeok), KNO_2 (≥96.0 wt%, Sigma-Aldrich) or KNO_3 (≥99.0 wt%, Sigma-Aldrich). After 30 min surface modification at the open-circuit potential (OCP), the electrode was gently cleaned twice in pure 0.1 M KOH solution to remove unadsorbed NO_x species and then transferred to the blank or NH_3 electrolyte. During the cleaning and transfer steps, the meniscus-like thin liquid layer naturally formed on the Pt electrode was retained to protect the adsorbates from air. Stripping and AOR analyses were performed by CV in the potential range 0.05–1.2 V_{RHE} at a scan rate of 50 $mV\,s^{-1}$. Combined stationary/transient polarization curves were recorded by linear-sweep voltammetry (LSV) from 0.05 V_{RHE} to the upper potential limits (E_{UPL}), holding the potential at E_{UPL} for t min followed by LSV to 0.05 V_{RHE} (E_{UPL} = 0.4–1.2 V_{RHE}, t = 0–5 min). A scanning flow cell (SFC) combined with a mass spectrometer (Max 300 LG, Extrel) was used for the DEMS study [22]. The SFC with U-shaped channels had an opening diameter of 1 cm at the bottom of the cell, where it made contact with the working electrode. At the top of the cell, a tip with a porous Teflon membrane at the end was introduced and positioned ca.100 μm above the working electrode, allowing introduction of volatile products directly into the mass spectrometer. The potential was changed from 0.05 to 1.2 V_{RHE} with a scan rate of 5 $mV\,s^{-1}$, and concurrently the NO ($m/z = 30$) and N_2O ($m/z = 44$) signals were detected. To remove N_2O contributions at $m/z = 30$, the initial signal from $m/z = 30$ was corrected by subtracting of 27% signals from $m/z = 44$.

3. Results and discussion

3.1. Stripping of the NO_x-adsorbed Pt surface

Cyclic voltammograms of the bare and NO_x-adsorbed Pt electrodes are shown in Fig. 1a–d. In a blank electrolyte, the OCPs of the Pt electrodes with NO_x adlayers are ca. 0.92 (±0.03) V_{RHE} higher than that of the bare Pt electrode (ca. 0.67 V_{RHE}), indicating changes in the Pt surface chemistry after NO_x-adsorption. Two different stripping methods were used in this study, with the potential cycling beginning from the OCP with an initial anodic or cathodic scan. In both measurements, the stripping results on the Pt electrode with a NO adlayer show broad reduction currents below the OCP and peaks at ca. 0.17 V_{RHE} (Fig. 1a and b). Similarly, the Pt electrodes with NO_2^- and NO_3^- adlayers also show broad reduction profiles at potentials below the OCP and peak maxima at ca. 0.19 V_{RHE}. These reactions have been associated with $*NO_x$ reduction to N_2, NH_3 or NH_2OH in previous works [23–28].

In the stripping CV with initial cathodic scan, the calculated coulometric charge density (σ), corrected by the bare Pt electrode charge, is ca. 392 $\mu C\,cm^{-2}$ for *NO reduction (σ_{NO}^-, where superscript and subscript denote the direction of the initial potential scan and species of the adsorbate, respectively; Fig. 1e). This is in good agreement with the value of 367 $\mu C\,cm^{-2}$ reported by De Vooys et al. [23]. Assuming that the only product from the reductive *NO stripping is NH_3 [23,24], the σ_{NO}^- value corresponds to a reasonable coverage of ca. 0.37 (slightly higher than De Vooys' value of 0.34, probably due to the imperfectly flat surface of the Pt electrode). In $*NO_2^-$ and $*NO_3^-$ stripping analyses, the $\sigma_{NO_2^-}^-$ and $\sigma_{NO_3^-}^-$ values are ca. 349 and 304 $\mu C\,cm^{-2}$ (Fig. 1e), respectively, while their coverages cannot be calculated because of the multiple products of the reactions [25–28]. As compared with the $\sigma_{NO_x}^-$ values, those measured from the initial anodic scan ($\sigma_{NO_x}^+$) changed insignificantly (i.e. $\Delta\sigma(\%) = 100 \times (\sigma^+ - \sigma^-)/\sigma^- < \pm 20\%$; Fig. 1b and e). This result indicates that considerable NO_x adlayers remain adsorbed on the Pt surface after the initial anodic scan up to 1.2 V_{RHE}, although the $*NO_x$ species can be transformed to further oxidized forms at this high potential (e.g. $*NO \rightarrow *NO_2^- \rightarrow *NO_3^-$) [28–35].

The effects of the NO_x adlayers on the AOR activity of the polycrystalline Pt were then studied in the NH_3 electrolyte (Fig. 1c and d). The AOR on bare Pt shows an onset potential of ca. 0.5 V_{RHE} and a peak maximum at ca. 0.7 V_{RHE}, consistent with those of polycrystalline Pt electrodes reported previously [7,15]. However, the Pt electrodes with NO_x adlayers exhibit very different AOR properties. In the first CV cycle with the initial anodic scan (Fig. 1d), the AOR peaks are considerably decreased in intensity and anodically shifted. The NO_2^- and NO_3^- adlayers introduce more significant decreases in AOR activity than the NO adlayer. These results indicate that all three NO_x species adsorbed on Pt can behave as site-blocking agents, thus impeding efficient recombination of $*NH_x$ species to N_2. This first finding directly supports many recent suggestions proposed by advanced in situ/online spectroscopic analyses [14,15].

In the first CV cycle with the initial cathodic scan in the NH_3 electrolyte (Fig. 1c), reduction of the NO_x adsorbates occurs in a broad potential range below the OCPs, with peak maxima at ca. 0.16 V_{RHE}. The $\sigma_{NO_x}^-$ values measured in the NH_3 electrolyte are 346, 348 and 271 $\mu C\,cm^{-2}$ for adsorbed NO, NO_2^- and NO_3^- (Fig. 1e), respectively, similar to those measured in the blank electrolyte. After the reductive stripping, the AOR activity of the NO_x-adsorbed Pt electrodes is recovered, indicating the removal of NO_x adlayers through reduction [36,37]. However, the CVs of the NO_x-adsorbed Pt electrodes with the initial anodic scan show nearly identical voltammetric profiles to that of the bare Pt electrode at potentials of > 0.3 V_{RHE} in subsequent cathodic scan (i.e. no additional reduction reaction; Fig. 1d). Reductive peaks are observed at ca. 0.16 V_{RHE}, but the $\sigma_{NO_x}^+$ values, calculated from differences of the reduction profiles between the bare and NO_x-adsorbed Pt electrodes, are only 124, 47 and 10 $\mu C\,cm^{-2}$ (i.e. $\Delta\sigma = -64$, -86 and -96%) for adsorbed NO, NO_2^- and NO_3^- (Fig. 1e), respectively. This substantial change can hardly be ascribed to the oxidation of the NO_x adlayers and consecutive desorption from the Pt surface, because identical measurements in the blank electrolyte show no significant changes in the σ values.

This led us to suggest that the $*NO_x$ species can react with NH_3 (or $*NH_x$) and be removed from the Pt surface. This second finding is consistent with the Langmuir–Hinshelwood mechanism of AOR, in which chemical N—N coupling reaction between $*NH_x$ and *NO species causes the formation of N_2 [28,38]. Duca et al. reported that *NO is a key intermediate of the coupling reaction, and thus the removal of $*NO_2^-$ (and reasonably $*NO_3^-$) should be preceded by their reduction to *NO [28]. Based on this reaction mechanism, it seems reasonable to surmise that in Fig. 1d the higher AOR activity on the NO-adsorbed Pt electrode compared to the NO_2^-/NO_3^--adsorbed ones is probably due to the relatively efficient removal of *NO through formation of N_2 during the first anodic scan, which provides catalytically available Pt sites.

3.2. Formation of $*NO_x$ species on Pt surface

Combined stationary/transient voltammetric analyses, typical CVs with the potential held at E_{UPL} for a certain time (Fig. 2a), were performed on the bare Pt electrode in the NH_3 electrolyte. For the potential plateaus of E_{UPL} > 0.7 V_{RHE}, the AOR current density decreased rapidly (data not shown). Thereafter, subsequent transient voltammetry revealed accumulated unknown adsorbates on the Pt surface, as evidenced by higher reduction currents than those observed without the potential hold (Fig. 2b–g). Adsorbate reduction was more apparent at E_{UPL} > 0.8 V_{RHE}. At this high potential, NH_3 oxidations to NO, NO_2^- and NO_3^- become thermodynamically possible (E° = 0.704, 0.648 and 0.695 V_{RHE}, respectively [14]). For instance, our online DEMS measurement during the AOR shows the evolution of volatile NO and N_2O