

NITRIC OXIDE REDUCTION AND OXIDATION ON POLYCRYSTALLINE PLATINUM: DIFFERENTIAL REFLECTANCE SPECTROSCOPIC STUDIES

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Nitric Oxide (NO) is a key intermediate in many environmentally and industrially important processes, such as nitrate reduction and ammonia oxidation.¹ NO has also been found to be a neurotransmitter and therefore there is great interest in developing electrochemical sensors for NO. Furthermore, the adsorption and reactivity of NO on transition metalsurfaces are of considerable interest from a fundamental viewpoint and could serve as a model system in electrocatalysis in general.

Recent studies of the electrochemical transformation of NO adlayers (NO_{ads}) on low-index single-crystal platinum electrodes²⁻⁴ have significantly improved our understanding of the reactivity of nitric oxide. However, various aspects of the dynamics of NO_{ads} reduction and oxidation still remain largely unknown. The primary objective of this work is to exploit the power of a variety of in situ spectroscopic techniques now available in our laboratories⁵ for gaining additional insight into these processes.

EXPERIMENTAL

Reflectance measurements were performed using a medium power (ca. 15-17 mW) HeNe laser (JDS Uniphase Model 1144P, 633 nm) as the light source. The setup was similar to that reported earlier in our laboratories.⁶ Measurements were performed at room temperature in Ar-purged (Praxair 5.0) ultrapure aqueous (18.3 MΩ water, Barnstead water purifier) 0.1 M HClO_4 (Ultrex) in an all-Teflon three electrode cell. A polished polycrystalline Pt disk electrode ($A = 0.164 \text{ cm}^2$) was used as the working electrode. A platinum wire and a SHE were used as counter and reference electrodes, respectively. Nitric oxide was prepared in situ by introducing NaNO_2 into the acidic solution which decomposes spontaneously to yield NO which then adsorbs irreversibly on Pt.

RESULTS AND DISCUSSION

Shown in Fig. 1 are cyclic voltammograms (upper panel) and normalized differential reflectance $\Delta R/R$ (lower panel) for a Pt disk electrode in 0.1 M HClO_4 recorded simultaneously in the presence (see black curves) and absence of nitrite in solution (See red curves, Fig. 1) nitrite in solution. In the absence of nitrite, the $\Delta R/R$ remains essentially constant in the hydrogen adsorption and double layer regions to later drop as the layer of oxide is formed. The adsorption of NO was found to elicit a significant drop in $\Delta R/R$ from that measured in pristine 0.1 M HClO_4 over the region 0.2 up to 0.8 V and to delay the onset of oxide formation to ca. 1.2 V (compare red and black lines in the lower panel in Fig. 1). In fact, inspection of the optical data indicates that the

onset for the oxidation current coincides with the drop in $\Delta R/R$ characteristic of oxide formation. For potentials lower than 0.2 V the optical signal increased monotonically to reach at 0.05 V values very similar to those found in the absence of nitrite in solution.

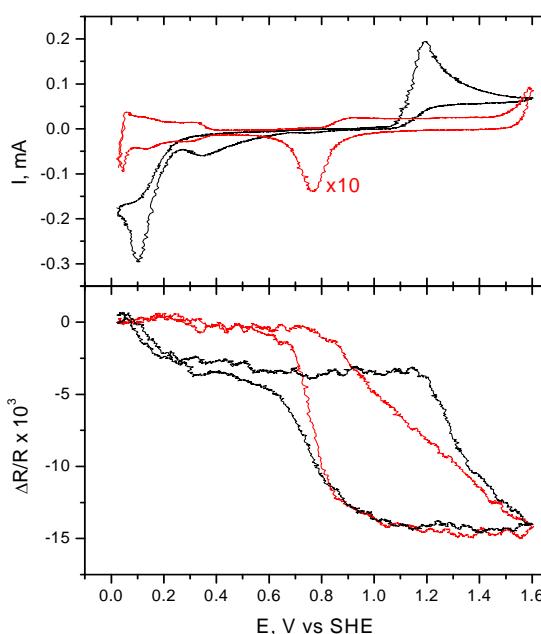


Fig. 1. Cyclic voltammograms (upper panel) and normalized differential reflectance, $\Delta R/R$ ($E_{\text{ref}} = 0.025 \text{ V}$) (lower panel), for a Pt disk electrode (Area: 0.164 cm^2) recorded simultaneously at a scan rate of 10 mV/s in 0.1 M HClO_4 in the absence (red) and presence (black) of 10 mM NaNO_2 .

ACKNOWLEDGEMENTS

This work was supported by a Grant from NSF.

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