



The oxidation of hydroxylamine on Pt-, and Pd-modified Au electrodes in aqueous electrolytes: Electrochemical and in situ spectroscopic studies

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ABSTRACT

The electrooxidation of hydroxylamine, NH_2OH , in 0.1 M phosphate buffer (PB, pH = 7) on Pt-, and Pd-modified Au electrodes prepared by galvanic displacement of underpotential deposited Cu, was investigated by electrochemical techniques and three and in situ vibrational probes, substrate-induced surface enhanced Raman scattering, SI-SERS, surface enhanced infrared absorption, SEIRAS, and Fourier transform infrared reflection-absorption, IRAS, spectroscopies. Analyses of the results obtained made it possible to identify at low overpotentials, solution phase (sol) and adsorbed (ads) nitric oxide, NO, as well as solution phase nitrous oxide, N_2O . As the potential was increased, the peak(s) ascribed to NO(ads) gained in intensity and new features associated with $\text{NO}_2^-(\text{ads})$ and $\text{NO}_2^-(\text{sol})$ were clearly discerned. Further excursion toward higher potentials yielded an additional peak assigned to $\text{NO}_2(\text{ads})$. This behavior is analogous to that found for bare Au electrodes in a potential region in which the metal is at least partially oxidized under otherwise the same experimental conditions.

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1. Introduction

Continuing efforts in our laboratories [1–5] are being aimed toward gaining insight into the factors that control the electrochemical properties of species involved in the nitrogen cycle in aqueous electrolytes [6], including the effects associated with the nature of the electrode and pH. Our attention has been focused primarily on the electrooxidation of hydroxylamine, NH_2OH , on Au, which, until recently, was believed to be electrocatalytically inactive for this specific process. In particular, we have unambiguously established that one of the main products generated at small overpotentials is solution phase nitric oxide NO [3], a species that exhibits no affinity for Au [7]. In marked contrast, strong spectroscopic evidence has been found for the presence of adsorbed NO both on polycrystalline [8,9] and low index face single crystal Pt surfaces [10,11] in acidic electrolytes over a wide potential range. It is therefore of fundamental interest to examine the influence of this adsorbed intermediate on the overall reaction mechanism of NH_2OH oxidation. This contribution presents the results of an integrated electrochemical and in situ vibrational study including substrate-induced surface enhanced Raman scattering, SERS, surface enhanced infrared absorption, SEIRAS, and Fourier transform infrared reflection-absorption spectroscopies, IRAS, for the oxidation of NH_2OH on Au electrodes modified by a monolayer of either

Pt or Pd assembled by galvanic displacement of underpotential deposited Cu.

2. Experimental

2.1. Electrochemistry

All measurements were performed in Ar (UHP, 99.999%, Air-gas) – deaerated NH_2OH (Aldrich, 99.999% pure) solutions in 0.1 M phosphate buffer (PB, pH = 7), prepared from $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ (Baker, Ultrapure Bioreagent, 99.9% pure), Na_2HPO_4 (Baker, Ultrapure Bioreagent, 99.7% pure) and ultrapure water (UPW, 18.3 M Ω cm, EASYpure UV system, Barnstead). Experiments under forced convection were conducted with a rotating Au (disk)|Au(ring) electrode, RRDE (Pine Instruments, disk diameter: 0.457 cm; ring outer diameter: 0.538 cm; ring inner diameter: 0.493 cm; disk area, $A_{\text{disk}} = 0.164 \text{ cm}^2$; ring area, $A_{\text{ring}} = 0.037 \text{ cm}^2$; gap, $G = 180 \mu\text{m}$; collection efficiency, $N = 0.22$) using a commercial rotator (Pine Instruments, Model AFMSRX) and a bipotentiostat (Pine Instruments, Model AFCBP1). Experiments were carried out at room temperature (23 °C) in a conventional all-glass, three-compartment cell with a standard hydrogen electrode (SHE) in 0.5 M H_2SO_4 (Fisher, ACS, 96.7%) prepared as described elsewhere [12], as a reference, and a gold wire as a counter electrode. Both Pt-, and Pd-modified Au surfaces were prepared by galvanic displacement as described by Mrozek et al. [13] This method involves, as a first step, the formation of a monolayer of Cu on Au by underpotential deposition (upd) from a 1 mM CuSO_4 (Fisher, ACS, 100.7% as

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$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) solution in 0.1 M H_2SO_4 performed by scanning the potential from 0.8 V vs SHE down to a value just positive to the onset of Cu bulk deposition. After holding at this potential for 30 s, the $\text{Cu}(\text{upd})/\text{Au}$ surface is removed from the solution under potential control and immediately immersed into deaerated solutions of either 5 mM K_2PtCl_4 (Aldrich, 99.4% pure) or 5 mM PdCl_2 (Alfa Aesar, 99.9% pure) in 0.1 M HClO_4 and left there for 10 min. During this period, the noble metal replaces Cu on the Au surface forming a robust monolayer, which is then rinsed thoroughly with UPW prior to use.

2.2. In situ surface enhanced Raman scattering (SERS)

SERS spectra were recorded with a commercial Raman system (Sentinel – CHROMEX, Bruker, 785 nm, 70 mW) using a quartz cuvette (Spectrosil® Far UV Quartz, Starna) as the main electrochemical cell compartment. The power at the sample, as measured with a power meter, was of ca. 25 mW. For these measurements, a Au electrode was prepared by first grinding a Au sphere – formed by melting a wire (Alfa Aesar, 99.999% pure) – encased in glass, using silicon carbide paper (Carbimet 2 – grit 400/P800, Buehler) until a circle of cross sectional area of ca. 0.025 cm^2 was exposed, and later polished with a finer paper (Microcut P4000, Buehler). After sonication in UPW for 5 min, the Au disk was roughened electrochemically by the method reported by Gao et al. [14], which involves application of 25 oxidation–reduction cycles generated with a programmable EG&G PAR Model 273 Potentiostat/Galvanostat in aqueous 0.1 M KCl (Fisher, ACS, 99.9% pure) between -0.3 and $+1.25$ V vs SCE at sweep rates of 1 and 0.5 V s^{-1} for scans toward positive and negative values, respectively. After each linear scan, the potential was held at the positive and negative limits for 1.2 and 30 s, respectively. Following thorough rinsing, these Au electrodes yielded optimal SERS activity and stability.

Platinum-, and Pd-modified Au surfaces were prepared by the same method described in the previous subsection. In situ SERS spectra of metal-modified Au and also bare Au were collected in 1 mM NH_2OH in PB using a Au wire and a SHE as counter and reference electrodes, respectively. Potentials were controlled by a Pine bipotentiostat (RDE3). Spectra were collected in ascending or descending sequence at fixed potentials, using a linear scan (50 mV^{-1}) to reach each successive value. This quasi staircase protocol was also employed for the acquisition of in situ infrared spectroscopy data. Each of the in situ SI-SERS spectra presented in this work was collected over a period of 60 s.

2.3. In situ infrared spectroscopy

All infrared spectra were recorded with a Bruker (Tensor 27) FT-IR spectrometer equipped with a narrow-band MCT detector (Infrared Associates) with either unpolarized (SEIRAS) or p-polarized light (IRAS) at a resolution of 4 cm^{-1} .

2.3.1. Surface enhanced IRAS (SEIRAS)

These experiments were performed in the so-called Kretschmann configuration [15], using a non-doped Si hemicylinder (Edmund Optics Inc.). The flat surface of this optical element was first polished with alumina compounds down to $0.3 \mu\text{m}$ (MicroPolish® alumina, Buehler), sonicated in acetone and water, and then hydrogen terminated by placing it in contact with a 40% NH_4F (Fisher, ACS, 99.1% pure) aqueous solution for 15 min to remove the native oxide layer. A very thin film of Au was then deposited by placing on this carefully prepared Si surface several drops of an aqueous solution containing two parts of a mixture of 0.015 M $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Aldrich, 99.9% pure), 0.15 M Na_2SO_3 (Fisher, ACS, 98.3% pure), 0.05 M $\text{Na}_2\text{S}_2\text{O}_3$ (Mallinckrodt) and 0.05 M NH_4Cl (Fisher, ACS, 99.9% pure), and one part of a 2% (v/v) HF (Acros Organics, 48–51%) aqueous solution [16]. The mixture was kept on the hydrogen terminated Si surface at 60°C for 90 s, then washed copiously with UPW, and finally cleaned by electrochemical cycling between -0.55 and 1.55 V in PB until a stable cyclic voltammogram was obtained. The same galvanic displacement procedure described in Section 2.2 was used to prepare Pt-, and Pd-modified Au films supported on the Si prism surfaces.

2.3.2. Infrared reflection absorption spectroscopy (IRAS)

The spectroelectrochemical cell used for these experiments, described in detail elsewhere [17], incorporates a polycrystalline Au foil encased in Kel-F (area: ca. 1.7 cm^2) working electrode, a thin Au foil counter electrode and a flat CaF_2 window. During spectral acquisition, the working electrode was pressed against the flat surface of the window using a micrometer in order to reduce the thickness of the electrolyte in the path of the IR beam. Each spectrum presented in this work represents the average of 100 consecutive interferometric scans.

3. Results and discussion

3.1. Electrochemistry

Shown in Fig. 1 are cyclic voltammograms recorded at a scan rate, $\nu = 10 \text{ mV s}^{-1}$, in deaerated PB under quiescent conditions with

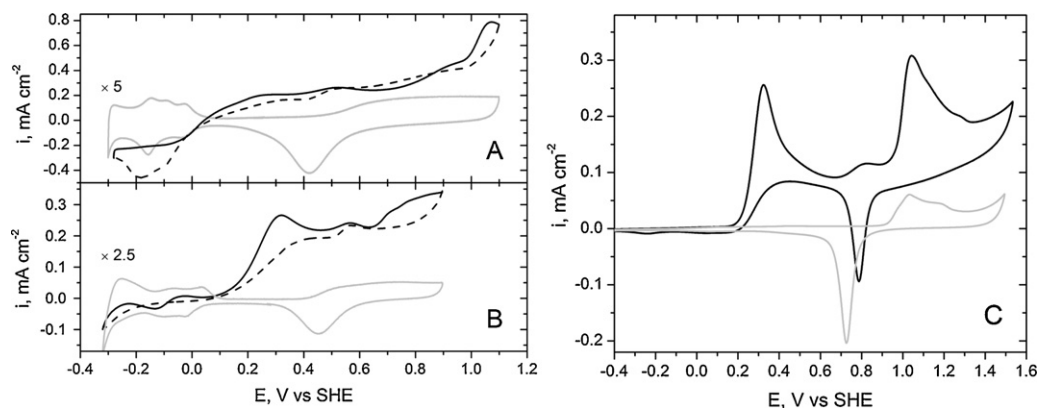


Fig. 1. Cyclic voltammograms ($\nu = 10 \text{ mV s}^{-1}$) of a Pt-modified (Panel A) and Pd-modified (Panel B) Au disk of a Au|Au RRDE in 0.1 M phosphate buffer (PB, pH = 7) in the presence (black curves) and in the absence (gray curves) of 2 mM NH_2OH in the solution. Corresponding data collected for the bare Au disk is shown in Panel C. The dashed lines were collected during the scan toward negative potentials.

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