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Electrocatalytic properties of adsorbed halides: The reduction of hexaaquairon(III) on polycrystalline gold in aqueous electrolytes

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ABSTRACT

Enhancements in the rates of reduction of hexaaquairon(III), $[Fe(H_2O)_6]^{3+}$, on polycrystalline Au, Au(poly), induced by the adsorption of bromide, Br^-, have been examined by chronoamperometric techniques in 0.1 M $HClO_4$ aqueous solutions containing Br^- at concentrations in the μM (< 1 ppm) range using a Au(poly)|Au (poly) rotating ring|disk electrode, RRDE. The extent of Br^- adsorption on the Au(poly) disk was determined quantitatively by monitoring the diffusion-limited current for the oxidation of Br^- on the Au(poly) ring in solutions devoid of $[Fe(H_2O)_6]^{3+}$. Evidence that Br^- adsorption is not affected by the reduction of $[Fe(H_2O)_6]^{3+}$ was obtained from in situ differential reflectance measurements performed in the absence and in the presence of the metal complex in solution. Information derived from these measurements was then used to establish quantitative correlations between the disk current, i_{disk}, associated with the reduction of $[Fe(H_2O)_6]^{3+}$ and E, at constant $\theta_{Br}{}^N$, and between i_{disk} and the normalized Br^- coverage, $\theta_{Br}{}^N$, at constant potential, E. Rather surprisingly, significant increases in electrocatalytic activity over the otherwise bare Au (poly) surface could only be discerned for $\theta_{Br}{}^N > 0.15$. Possible explanations for this unexpected behavior are discussed.

1. Introduction

The influence of adsorbed species on the kinetics and mechanism of a number of redox reactions has been recognized for decades and continues to be the subject of numerous studies of both fundamental and technological importance [1].This contribution provides a quantitative measure of the extent to which adsorption of a halide affects the rates of a simple redox process involving solution-phase species, using the reduction of hexaaquairon(III), $[Fe(H_2O)_6]^{3+}$, on a polycrystalline Au electrode, Au(poly), in aqueous 0.1 M $HClO_4$ containing bromide, Br^-, as a model system [2]. Perchlorate ion displays very weak affinity for Au surfaces [3] and, as such, may be regarded as uniquely suited for these studies. The specific strategy employed in this investigation, described in detail in a recent communication [4], is based on a combination of chronoamperometric, optical and rotating ring-disk electrode, RRDE, techniques that allow the time evolution of the Br^- coverage to be determined while the redox process is taking place. Although some aspects of this methodology share some common features with tactics reported earlier in the literature [2a,5], there are important differences that makes it particularly advantageous. Specifically,

i. the disk of the RRDE electrode is first polarized *under rotation* at a potential, E_o, negative enough to induce the full desorption of Br^-, and then stepped to a potential E_{step}, at which adsorption of Br^- is expected to ensue under strict diffusion control for times up to tens of seconds.
ii. The flux of bromide to the disk, and, thus, the absolute amount of Br^- adsorbed on the disk is determined from the shielding of the diffusion-limited ring current associated with Br^- oxidation [5], and, as such, avoids uncertainties associated with the analysis of the disk current.
iii. In situ optical differential reflectance is used to monitor adsorption of Br^- on the disk to confirm that the redox reaction does not interfere with the Br^- adsorption process.

An illustration of the power of this technique was provided recently by Jebaraj et al. [4], who examined the effects of Br^- adsorption of Pt (poly) on the reduction of oxygen and hydrogen peroxide in aqueous 0.1 M $HClO_4$ solutions. As will be shown, correlations between i_{disk} and the normalized Br^- coverage, $\theta_{Br^-}{}^N$, for various values of E_{step}, revealed that significant enhancements in the electrocatalytic activity of Au (poly) for the reduction of $[Fe(H_2O)_6]^{3+}$ could only be discerned for $\theta_{Br^-}{}^N < 0.15$.

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2. Experimental

All measurements were performed in an all-glass, three-compartment cell, filled with deareated (Ar, UHP, 99.999%, Airgas) 0.1 M $HClO_4$ solutions (75 mL) prepared from ultrapure perchloric acid (Ultrapure, EMD), and ultrahigh purity, UHP, water generated by a Barnstead system (18.3 MΩ cm, EASYpureUV), either neat or containing 10 μM KBr (Fisher Scientific, IR grade, > 99%), and/or hexaaquairon(III) perchlorate hydrate ($Fe(ClO_4)_3{\cdot}xH_2O$, Sigma Aldrich, < 0.1% chloride), as received. Experiments were carried out with a Au(poly)|Au(poly) RRDE working electrode (Pine Instruments, disk radius: 0.2285 cm; ring inner diameter 0.2465 cm; gap, G = 180 μm and ring outer diameter 0.2690 cm, or, correspondingly, disk and ring areas of 0.164 cm^2 and 0.037 cm^2, respectively, and a collection efficiency, N = 0.22). A carbon rod and a reversible hydrogen electrode (RHE) were used as counter and reference electrodes, respectively. The disk and ring potentials, E_{disk} and E_{ring}, respectively, were controlled with a bipotentiostat (Pine Instruments, Model AFCBP1) and the rotation rate of the RRDE, ω, was adjusted with a commercial rotator (Pine Instruments, Model AFMSRX). All the data were recorded using an acquisition card (National Instruments, USB-6009) programmed in Labview. Cyclic voltammetric curves recorded in deareated 0.1 M $HClO_4$ at ω = 400 rpm yielded features characteristic of clean Au(poly) surfaces.

Normalized optical differential reflectance measurements, $\Delta R/R = [R(E_{ref}) - R(E_{sam})] / R(E_{ref})$, where $R(E_{ref})$ and $R(E_{sam})$ represent the intensity of the light collected at the detector following reflection from the Au electrode polarized at a reference, E_{ref}, and an arbitrary sampling potential, E_{sam}, respectively, were performed using a blue diode laser (Polaris 700, λ = 447 nm, 900 mW, Laserglow), while collecting chronoamperometric data employing methods and instrumentation specified in detail elsewhere [4]. Chronoamperometric experiments were carried out for fixed [Br^-] and variable ω. In all instances, the disk current, i_{disk}, was monitored following application of a potential step from $E_o = -0.15$ V, i.e. no Br^- adsorption, to values of E_{step} in the range $0.0 \le E_{step} \le 0.9$ V vs RHE, i.e. negative to the onset of oxide formation on Au(poly) in neat 0.1 M $HClO_4$, and to the onset of $[Fe(H_2O)_6]^{3+}$ reduction (vide infra).

3. Results and discussion

Shown in Fig. 1 (left ordinate) are dynamic polarization curves collected with the disk of the Au(poly)|Au(poly) RRDE in the absence (red) and presence (black) of 10 μM KBr in deaerated 0.1 M $HClO_4$ containing 1 mM $Fe(ClO_4)_3$ at a scan rate ν = 10 mV/s and a rotation rate ω = 400 rpm. The dash-dotted gray line in this figure is the difference between the red and black lines, which serves to illustrate the ability of adsorbed Br^- to catalyze the reduction of $[Fe(H_2O)_6]^{3+}$, and the arrow indicates the direction of the scan.

Correlations between the coverage of bromide, θ_{Br}, on the Au(poly) RDE and its activity for the reduction of $[Fe(H_2O)_6]^{3+}$ were sought by first using the method of Gasteiger et al. [5] to determine the extent of Br^- adsorption in the absence of the redox couple in solution. This tactic relies on measurements of the ring currents associated with Br^- oxidation under diffusion limited conditions following application of a potential step to the disk from a value negative enough to induce full desorption of Br^-, E_o, to a higher value, E_{step}, at which adsorption of Br^- on the disk is expected to ensue. The results of these experiments are given in Section 3.1 below. Also included therein are in situ optical data that affords evidence that, θ_{Br} values obtained in the absence of $[Fe(H_2O)_6]^{3+}$ are applicable when analyzing the reduction of the complex (see Section 3.2).

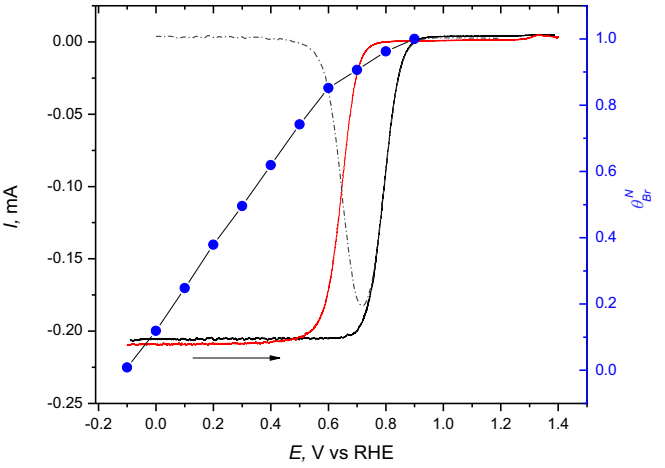

Fig. 1. Dynamic polarization curves (left ordinate) collected with the Au|Au RRDE in the absence (red) and presence (black) of 10 μM KBr in deaerated 0.1 M $HClO_4$ containing 1 mM $Fe(ClO_4)_3$ at ν = 10 mV/s and ω = 400 rpm, where the arrow specifies the direction of the scan. The dash-dotted gray line is the difference between the red and black lines. The blue scattered symbols (see right ordinate) represent normalized values of the bromide coverage, $\theta_{Br}{}^N$ (see text). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

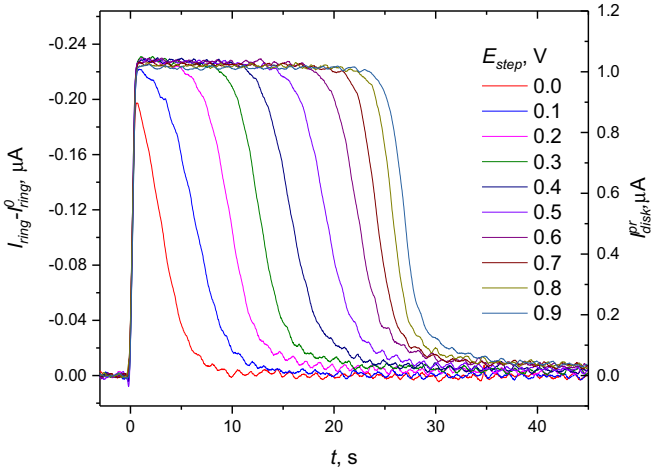

Fig. 2. Plots of $I_{ring} - I_{ring}{}^o$ vs time recorded with the Au ring of a Au|Au RRDE polarized at E_{ring} = 1.4 V vs RHE, during the acquisition of the chronoamperometric disk data in 10 μM KBr in 0.1 M $HClO_4$ at ω = 400 rpm, by stepping the Au disk potential at t = 0 from $E_o = -0.15$ V to various E_{step}, as indicated in the legend.

3.1. Bromide adsorption under forced convection: chronoamperometric studies

Shown in Fig. 2 (see left ordinate), are plots of the Au ring currents, I_{ring}, collected with the ring polarized at E_{ring} = 1.4 V vs RHE, a value positive enough, E_{step}, to oxidize Br^- under strict diffusion control, for a series of values in the range $0.0 \le E_{step} \le 0.9$ V. These transients can be used to determine the flux of Br^- associated with its adsorption on the Au disk, and following integration the number of mol of bromide adsorbing on the disk, $n_{disk}{}^{ads}$. The main advantage of this tactic is that the ring measures exclusively the amount of bromide adsorbing on the disk, regardless of the charge associated with the adsorption process, and would not contain contributions to double layer charging, as would be the case with the disk current. It should be stressed that the diffusional flux is a function of the cross sectional area of the electrode, whereas the actual number of ions adsorbed depends of the actual area of the