

Figure 2 Analysis of photocurrent measurements from excitation of AQI at 417 nm for light intensities (o) 1.7, (x) 3.7 (+) 8.2 (∆) 18.0 and (∇) 39.9 mWcm⁻².

On the basis of the extinction coefficients cited above it can be seen that the rate of iodide expulsion is 7.4 (± 0.9) times lower per photon absorbed at 417 nm than at 565 nm.

CONCLUSION

Channel electrode studies have shown that the photo-reduction of AQI proceeds via a mixed ECE/DISP1 mechanism and the kinetics of iodide expulsion has been quantified. It has been found that the different excited states of the AQI radical anion, obtained through excitation at either 417 or 565 nm, show different dynamic behaviour. In particular expulsion is some 7.4 times faster per photon absorbed with 565 nm radiation than with 417 nm. Further work, quantifying excited state lifetimes and spin densities, will seek to explain this behaviour.

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APPLICATION OF IN-SITU SNIFTIRS TO THE STUDY OF THE ELECTROREDUCTION OF DIOXYGEN ON GOLD

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This communication reports preliminary results obtained in a study of the electroreduction of dioxygen on different electrode materials applying in-situ SNIFTIRS. With this study we hope to be able to characterize the material surface in the absence of O₂ and to detect and characterize intermediates of the electroreduction reaction. We started by examining O₂ reduction on gold in alkaline solutions. In our experiments we used a thin layer cell with a CaF₂ window and a 7 mm diameter, 3 mm thick Au disc mounted in a teflon body. Saturated calomel and Hg/HgO electrodes were used as reference electrodes, but hereafter potentials are referred to RHE, the reversible hydrogen electrode (0 V/SCE = 1.06 V/RHE and 0 V/Hg/HgO = 0.94 V/RHE). Spectra were collected using a Biorad FTS-40 spectrometer interfaced to a 6800-based microcomputer supplied by OxyS Micros. In the following figures the ordinate represents the reflectance measured at a given potential and wavenumber relatively to the reflectance measured at a reference potential and the same wavenumber. Features pointing up, i.e. to relative reflectance > 1, correspond to a loss of the starting material, whereas features going down, i.e. to relative reflectance < 1, correspond to gain of a product.

Two types of experiments were carried on:

a) In one of them the reference spectrum was taken at 1.11 V (chosen as the potential where O₂ is not reduced); then the potential was stepped to successively more cathodic values and further spectra were collected. These spectra are shown in Fig 1 ratioed to the reference spectrum.

The spectra show two main loss features at ≈ 1660 and ≈ 3150 cm⁻¹ and one main gain feature at ≈ 3800 cm⁻¹. We assign these two loss features to the loss of adsorbed water from the electrode surface; therefore the bands at 1660 and 3150 cm⁻¹ correspond respectively to the bending mode and to the O-H stretching mode of H₂O. The low frequency of this last band and its large width are characteristic of hydrogen-bonded water [1]; the shoulder at ≈ 3580 cm⁻¹ may be due

to non-hydrogen-bonded OH groups at the borders and surfaces of the hydrogen-bonded clusters [1]. This loss of water is then probably related to the breaking of H-bonds caused by an increasing population of cations (K^+) in the double layer as the electrode potential goes negative. We assign the band at $\approx 3800\text{ cm}^{-1}$ to the stretch mode of adsorbed OH. The intensity of this band first increases up to $\approx 860\text{ mV}$ (-200 mV/SCE) and then decreases as the potential goes negative. This finding is in agreement with data obtained in cyclic voltammetry experiments on different surfaces of gold [2].

b) In another series of experiments, spectra were taken at time intervals of 35 s (the time needed to run 100 scans) at each of two fixed potentials (780 mV and 280 mV) after the admission of a O_2 -saturated 0.7 M KOH solution; immediately prior to this admission the reference spectrum was taken at 1.11 V with the gold electrode immersed in a N_2 -saturated 0.7 M solution. Solution transfers to the cell were performed using Schlenk techniques. These spectra are shown in Fig 2 a) and b).

The main features at 780 mV are gain features. We ascribe the band at $\approx 1250\text{ cm}^{-1}$ to perturbed adsorbed O_2^- [3], probably O_2^- that adsorbs with a certain charge transfer to the electrode surface. This evidence on the formation of O_2^- (ads) means that the mechanism previously suggested to account for the electroreduction of O_2 on gold in alkaline solutions [4] has to be modified accordingly. The band at $\approx 1400\text{ cm}^{-1}$ is due to CO_3^{2-} resulting from residual CO_2 in the gas line. Bands at ≈ 1640 , ≈ 2120 and $\approx 3060\text{ cm}^{-1}$ are due to HO_2^- , which is produced in the reduction reaction and goes into solution.

The band at $\approx 3430\text{ cm}^{-1}$ corresponds to a loss of bulk water.

The intensity of the bands decreases with time because of depletion of O_2 and diffusion of products out of the thin layer.

At 280 mV we observed the same gain features but the HO_2^- is shorter-lived. The loss of water is higher.

We also observed that two gain bands at 3680 and 3740 cm^{-1} develop with time at 780 mV but not at 280 mV. We tentatively ascribe these bands respectively to the symmetric and to the asymmetric O-H stretch of adsorbed OH^- produced during the disproportionation of HO_2^- .

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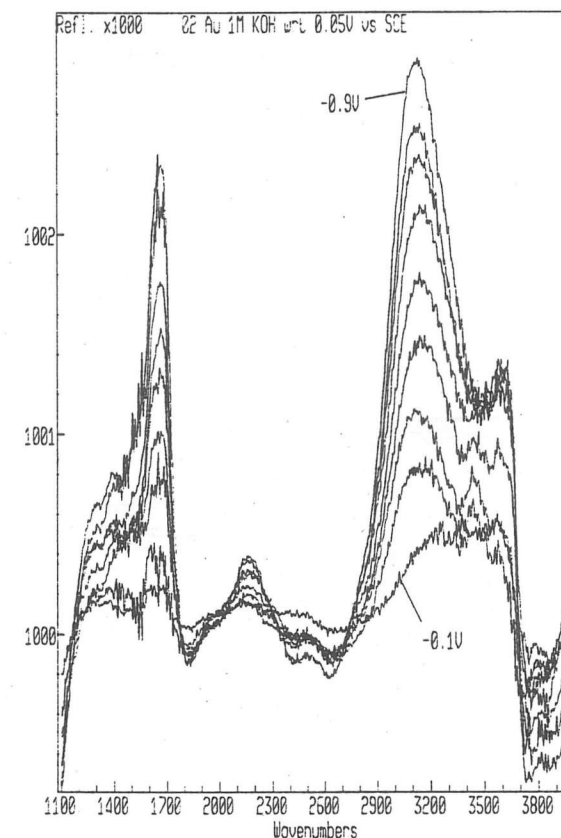


Fig 1. SNIFTIRS spectra taken off the Au electrode immersed in a N_2 -saturated 0.7 M KOH solution at several potentials and ratioed to the reference spectrum (taken at 0.05 V/SCE).

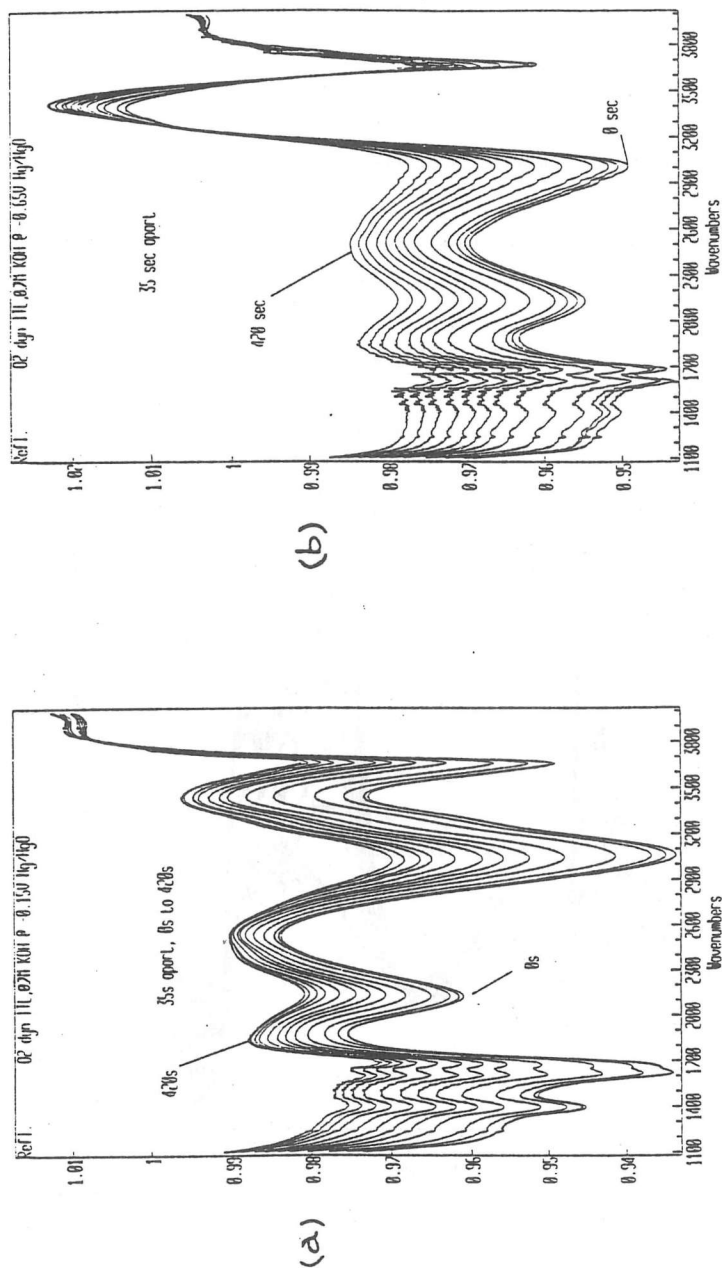


Fig 2. SNIFTIRS spectra taken off the Au electrode immersed in O₂-saturated 0.7 M KOH at (a) 780 mV/RHE and (b) 280 mV/RHE. Spectra were taken at various times after the admission of the O₂ solution and normalised to the reference spectrum taken at 1.11 V/RHE of the N₂-saturated 0.7 M KOH solution immediately prior to admission.

IN SITU INFRARED REFLECTANCE SPECTROSCOPY OF FORMALDEHYDE ADSORPTION ON POLYCRYSTALLINE PLATINUM ELECTRODES IN ALKALINE MEDIUM

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ABSTRACT

The oxidation of formaldehyde at platinum polycrystalline electrodes in alkaline solutions was investigated by Electrochemically Modulated Infrared Reflectance Spectroscopy (EMIRS). From the assignment of the IR absorption bands, adsorbed species were identified as linearly and bridge-bonded CO (poisoning intermediates), and as formate (reaction product).

INTRODUCTION

On the basis of cyclic voltammetry experiments, it was recently demonstrated that the oxidation of formaldehyde on platinum electrodes in alkaline solutions can occur through different processes, depending on potential, and that there is strong adsorption of intermediates in the hydrogen region (1,2). These strongly adsorbed species are oxidised in the potential range where a Pt(OH)_{ads} layer is formed. The determination of the number of electrons per site, N_{eps} , shows that these species can be identified as CO species both in the linear and bridge-bonded forms, characterized by N_{eps} of 2 and 1, respectively.

Furthermore, in aqueous solutions, formaldehyde is present as methylene glycolate, its hydrated form, the equilibrium constant of the dehydration reaction being about 10^{-3} (3). This shows that two active species are always in equilibrium in solution, and that the adsorption of methylene glycolate or its derivated forms onto the electrode surface must be considered. In this work some