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LETTERS

Electrochemical Production of H_2O_2 and O_2 at an Anthracene/H_2O Interface

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The discharge of electrochemically generated holes at an anthracene crystal/water interface produces mainly oxidation products of anthracene. At high current densities ($\sim$400 μA cm^{-2}), H_2O_2 and O_2 are produced. The efficiency of O_2 production is $\sim$3%.

It has previously been shown[1] that an electric current can be passed through an anthracene crystal provided with electrolytic contacts. Since the flow of current through the crystal occurs by electron movement, and ions carry the current in the aqueous phase, it follows that chemical oxidation and reduction of water must take place at the crystal/water interface. Jarnagin et al.[2] studied the chemical reactions that took place at this interface and found, paradoxically, that, at least for the discharge of the positive hole, not only was oxygen not produced, it was consumed. In this paper, we show for the first time that at sufficiently high current density, H_2O_2 and O_2 are produced at the crystal anode.

The experimental setup is shown in Figure 1. Anthracene single crystals were graciously donated by G. J. Sloan of DuPont Laboratories. In a typical experiment, the crystal was $\sim$500 μm thick, $\sim$0.48 cm^2 in effective area, and presented its ab plane to the aqueous contacting electrode. Holes were injected into the crystal at the cathode side of the crystal, using a 0.28 M Ce^{4+} solution in 12 M H_2SO_4. The holes were forced across the crystal under a field of 1×10^4 to 5×10^4 V cm^{-1} (300–1500 V), producing current densities of up to 430 μA cm^{-2}; the current density was kept contant within a factor of two during an experiment. The anode side of the crystal was in contact with 500 μL of HPLC grade H_2O, previously bubbled with ultrahigh purity N_2 (<1 ppm of O_2) to remove O_2. The external potential was applied between Pt electrodes I and II. The potential drop is negligible across the Ce^{4+} solution because the ionic strength is very high. The major potential drop is across the crystal, and a minor potential drop exists across the pure water electrode. An estimate of the voltage drop across the water electrode was obtained by moving Pt electrode II up to the anthracene surface in a typical experiment. It was found that, for an overall potential drop of 1000 V, about 60 V fall across the pure water. With time, this voltage drop is reduced because of the introduction of electrolytically generated polar organic materials into the water.

During the experiment, which could last as long as 1 h, O_2 was excluded by the use of rubber septa. Samples were extracted by means of a gas-tight syringe inserted through the rubber septum. Through the use of these techniques, the impurity O_2 concentration was greatly reduced, but it cannot be claimed that atmospheric O_2 was completely excluded from the anode side of the crystal. However, with

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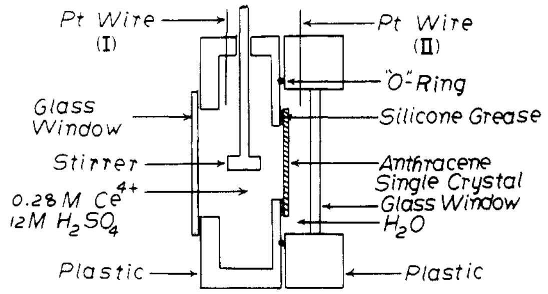

Figure 1. Cross section of electrolysis cell.

^{18}O labeled H_2O, it could be rigorously shown that the O_2 detected was produced by the electrolysis of the water.

After the passage of current, the solution was removed for analysis for H_2O_2 or O_2. H_2O_2 was identified through its ability to reduce ferricyanide to ferrocyanide[3] and by decomposition by the enzyme peroxidase.[4] Oxygen was determined by mass spectrometric analysis and by reaction with the dye viologen. In view of the fact that H_2O_2 converts easily to O_2, the only efficiency (ratio of the number of equivalents of O_2 per mole of carriers flowing in the external circuit) that can conveniently be measured is that of O_2 production.

As has been mentioned, there is a small, but indeterminate, amount of trace impurity in the system that is present because of incomplete purging. Thus, if one is interested in demonstrating that O_2 can be generated electrolytically in this system, the presence of tramp O_2 must be overcome. This is done by placing isotopically labeled water in compartment II; the composition used was 90% $H_2{}^{18}O$ and 10% $H_2{}^{16}O$. The gas produced during the electrolysis was analyzed in the mass spectrometer, and on the basis of the amount of $^{36}O_2$ found, an efficiency of O_2 production of 2–3% was calculated. The actual efficiency is somewhat higher, since the water was only 90% $H_2{}^{18}O$. Clearly the $^{36}O_2$ could only have been produced by the electrolysis of $H_2{}^{18}O$.

Although H_2O_2 is prepared commercially by bubbling O_2 into a solution of a derivative of anthracene (2-ethylanthraquinol),[5] atmospheric O_2 cannot be involved in the H_2O_2 production in this case because the isotopic content of the O_2 produced by the decomposition of H_2O_2 is that of the water. The production of O_2 was also monitored by its reaction with the dye methyl viologen.[6] The amount of O_2 indicated by the dye was in close agreement with that found by the mass spectrometer and increased linearly with total charge passed through the crystal. The major oxidation product on the anthracene surface is anthraquinone.

The electrolytic production of H_2O_2 at the anthracene anode proceeds through the recombination of OH radicals produced by the discharge of an OH^- by a hole at the crystal/water interface. The production of an OH· radical in water from the oxidation of an OH^- ion requires an energy of 6.8 eV,[7] referenced to the vacuum zero. The discharge of a hole in anthracene liberates about 5.9 eV,[8] so there is nominally a deficit of about 1 eV for the production of an OH· radical, if one disregards the as yet unknown potential energy jumps at the crystal/water interface. However, at high current densities, there appears to be a pileup of undischarged holes at the anode surface, resulting in a relatively large potential drop across the boundary layer. This potential drop would be the source of the energy necessary to raise the level of the reaction $OH^- + (+) \rightarrow OH\cdot$ to the level of the valence band in anthracene, where the electron on OH^- can tunnel into the valence band of the crystal. In addition to the OH· radical mechanism, holes can be discharged by means of a nucleophilic attack by water on the anthracene cation radical at the crystal/water interface, producing other oxidative derivatives of anthracene.

The chemical reactions that take place on the anthracene surface are complex and will be discussed in detail in a future publication.

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Surface Crystallography from Low-Energy Ion Backscattering Angular Distributions

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A new method for obtaining the arrangement of atoms at an ordered surface and for determining surface relaxations (to within 2% of interplanar spacings) by use of low-energy ions is presented. The method is illustrated with a computer simulation to generate the backscattered intensity distribution for 3-keV He^+ ions normally incident on a Cu(001) surface. When displayed on a position-sensitive detector, the total backscattered yield would reveal blocking-cone features that are real-space images of surface atoms.

Ion scattering spectroscopy (ISS) has been used for about 15 years in determining the elemental composition of solid surfaces.[1] More recently, many investigators have begun to use ISS to study the structural arrangement of atoms at surfaces as well.[2-6] Such research is still largely exploratory, and each experimental group has its own

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