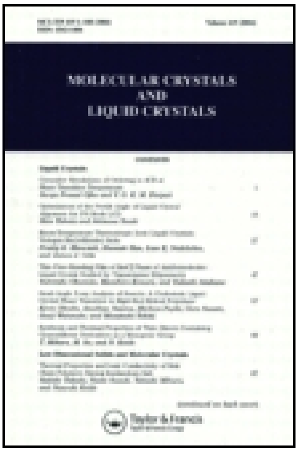

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Laser Interferometry of the Electrochemical Oxidation of Fe(II) in the Presence of Pyrrole

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Laser Interferometry of the Electrochemical Oxidation of Fe(II) in the Presence of Pyrrole

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Recent interest in the chemical route for the oxidation of pyrrole in order to produce conducting polypyrrole led to the investigation of the electrochemical oxidation of Fe(II) in the presence of pyrrole[1-4] using laser interferometry. The oxidation of pyrrole by aquo Fe(II) produces a polymer in solution whose dispersivity can be enhanced by having steric stabilizers such as polyvinyl alcohol-co-acetate, in the medium.[5] Each cluster of the charged polymer is presumably held in solution by electrostatic repulsion between the counter ions distributed in a diffuse layer surrounding each polymer. The above mechanism suggests the possibility of an electrocatalytic scheme for Fe(II) oxidation, provided that the chemical conversion rate can compete adequately with the electrochemical rate. The redox potential of Fe(II)/Fe(III) in aqueous medium is 0.77V[6] and is situated at a less positive value than the redox potential of pyrrole/pyrrole cation.[7] When this scheme is operating during an electrochemical oxidation, multiple beam laser interferometric fringe shifts are expected to be smaller as the local concentration of the product species, Fe(III), will be smaller by reaction with pyrrole[8] and the corresponding change in the medium refractive index will also be smaller at the electrode/solution interface. Alternatively, if Fe(II) or Fe(III) is incorporated during the reaction in a soluble state then one would expect a higher fringe shift, the extent of this shift being dependent on the refractive index of the new species. One report of Fe incorporating polymeric species has been prepared by a chemical route.[2] These possible situations have been examined for the electrochemical oxidation of Fe(II) in the presence of pyrrole.

EXPERIMENTAL

Laser Interferometric Studies were carried out by using an electrochemical cell and both multiple beam and real time holographic interferometry. The cell was filled with two semi-circular glass flats whose vertical cross sections were coated with Au by vacuum deposition for 5 min. The electrochemical cell was fitted into a square brass holder with three adjustable screws for the wedge angle. The cell itself acted as a Fabry-Perot interferometer. The electrodes were in the deep vertical configuration with the laser light travelling through the solution thickness which constituted the lesser dimension. The electrical contact to the electrodes was made through a copper wire pushed through the side ports to touch the Au contact to the semi-circular glass flat.

Ferrous chloride and ferric chloride used in this investigation were from BDH Analar grade. Pyrrole was obtained from Riedel and was purified by distillation. The fraction boiling at 132°C was used in the experiment. The galvanostatic electrolysis was carried out using a Keithley Constant Current Source (Model 220). The cell voltage was measured using a Keithley Digital Voltmeter.

The interferometric measurements were done using a He-Ne Laser (1 mW). The fringe movements were videotaped on a Hitachi video recorder (VTR Model VT-6500A) and were displayed on a 20" electroscan color television. A Hatachi VK-C870 microprocessor controlled video camera was used to follow the fringe patterns.

The holographic interferometry was carried out by procedures described earlier.[9,10] A 5 mW He-Ne laser beam (Spectra Physics, Model 120) was collimated to a beam splitter; the analysing beam passed through a glass cuvette fitted with two parallel Au plates (7.5 cm × 0.9 cm); the cell was mounted on a rigid plastic block fitted with two brass clamps. The reference beam was reflected on to a holographic plate by a mirror (Cohent Optics, Inc., Model 58) with adjustable tilts in the horizontal and vertical directions. The holographic plate was viewed through a telescopic lens attached to a 35 mm Nikon camera. The fringes were viewed with an RCA microprocessor controlled video camera (a Hitachi 5-head video recorder) attached to a Hitachi monitor in real time as each experiment progressed. The holographic set up was kept on an improvised pneumatic suspension table to minimize the building vibrations.

Cyclic voltammetric recordings were accomplished using a PAR 273 coupled to an Apple IIe computer. The current voltage curves were recorded using a Pt wire ($A \approx 0.14$ cm^2) electrode as the working electrode, Pt mesh as a counter electrode and a saturated calomel electrode as the reference electrode. An 'H' shaped cell was used for the measurements of the current-voltage curves.

Spectrophotometric recordings of the chemical reactions were carried out with a Perkin-Elmer Lambda 4B computered spectrometer.

RESULTS AND DISCUSSION

The electrochemical oxidation of aquo Fe^{2+} and the reduction of aquo Fe^{3+} in aqueous 1 N HCl were examined in the interferometric cell. The oxidation of 0.1M FeCl, produced an upturn of the fringes at the anode indicating an increase in the refractive index of the medium (n_{FeCl_3} = 1.34055 and n_{FeCl_2} = 1.34038). The progress of this electrolysis in the c.d.'s ranging from 0.2 mA cm^{-2} to 0.50 mA cm^{-2} was followed by a continuous video recording of the fringes and the exposure of a 35 mm film at selected intervals for analysis. The fringe shift ($\Delta F/F$) progressively increased as shown in Figure 1. This behaviour conforms well with an earlier report on Fe^{2+} oxidation in 1 N H_2SO_4 medium.[11] The electrochemical reduction of 0.1 M FeCl, in the interferometric cell exhibited a similar pattern but with a difference; the progress of the electrolysis was marked by a downturn of the fringes at the electrode surface signalling a decrease in the refractive index of the medium. At longer times >360S, a minor fringe shift decrease occurred due to the development of natural convection; this type of decrease is the characteristic of electrochemical reactions occurring at vertical electrodes.[11a] However, in the C/A position (cathode over anode) this type of behaviour was not observed.

The anodic oxidation of Fe(II) in the presence of 2.5 M pyrrole was also conducted at the above c.d.'s. The observed fringe shift displacement is shown in Figure 1 where the presence of pyrrole resulted in a higher fringe shift for Fe(II) oxidation during the electrolysis. The holographic fringes obtained during the above electrolysis are shown in Figure 2. The development of concentration—distance profiles in the two situations are markedly different, the diffusion layer is much more extended in the presence of pyrrole. A magnified diagram of the profiles is shown in Figure 3. The smoothness of the growth of the diffusion layer is nevertheless well defined.[12]

The chemical oxidation of pyrrole by Fe(III) was also examined by laser multiple beam interferometry. When 0.1 M $FeCl_3$ in 1 N HCl was mixed with 2.8 M pyrrole, the formation of a black polymer (see spectrophotometric results) occurred and if the solution was left overnight and filtered, the filtrate was a deep yellow. This solution

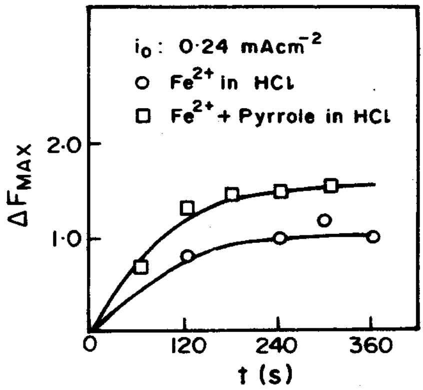

FIG. 1

FIGURE 1 Fringe shift during the electrolysis of 0.1 M $FeCl_2$ between two Au plated glass half discs. i_o: 0.24 mA cm^{-2}. $FeCl_2$ alone $FeCl_2$ with 28 m*M* pyrrole.

produced a black precipitate after standing for 2 hours due to agglomeration, suggesting the presence of pyrrole in the medium. The yellow solution (n = 1.34195) was examined by laser interferometry and Figure 4. shows the recorded fringe patterns; this recording was done within one half hour after filtration to separate the solidified polymer. Upturn of the fringes at the cathode and downturn of the fringes at the anode was observed and the fringe shifts increased

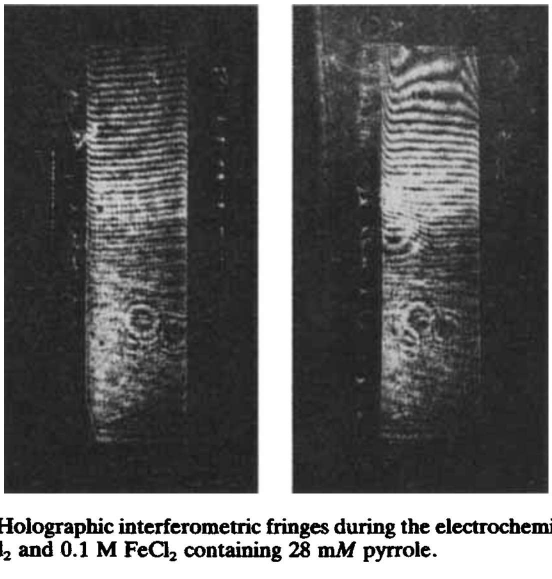

FIGURE 2 Holographic interferometric fringes during the electrochemical oxidation of 0.1 M $FeCl_2$ and 0.1 M $FeCl_2$ containing 28 m*M* pyrrole.

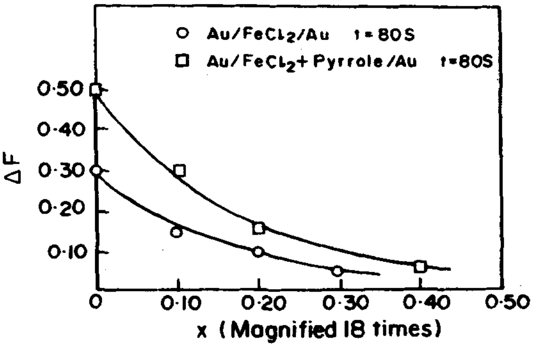

FIGURE 3 Development of concentration—distance profiles in the electrochemical oxidation of 0.1 M $FeCl_2$ at a c.d. of 0.12 mA cm^{-2}, and in the presence of pyrrole. Measurement made at t = 80 S.

progressively during the electrolysis. Assuming that a part of the Fe(III) (0.1 M $FeCl_3$) is converted to Fe(II) (in the simple mixing experiment) during a period of 24 hr, the fringe shift for a c.d. that matches the rate of chemical conversion ($\Delta C = \lambda/2kd \cdot \Delta F/F$, where λ is the wavelength of laser light, $k = dn/dc$ and d is the cell thickness; and $\Delta C_{(o,t)} = 2I/nFD^{1/2} \cdot t^{1/2}$ (0.595) where I is the current density, n is the number of electrons transferred, F is the Faraday, D is the diffusion coefficient and t is the elapsed time of electrolysis) cannot

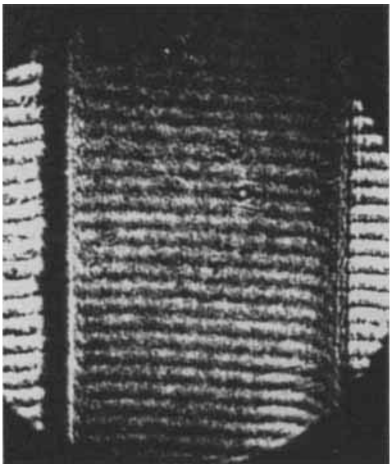

FIGURE 4 Multiple beam Laser Interferometry of the mother liquor solution of the reaction $FeCl_3$ and pyrrole obtained after standing for 24 hrs. Frame taken at a c.d. 0.59 mA cm^{-2} at 360 S.

be greater than the fringe shift for 0.1 M Fe(II) solution. Higher fringe shifts were therefore expected and observed for Fe(II) oxidation in the presence of pyrrole in the previous set of experiments.

Cyclic voltammetric results

The cyclic voltammetric curves for 10 m*M* aquo Fe(II) in 1 NHCl and for the same ion in the presence of pyrrole are shown in Figure 5. The absence of an electrocatalytic reaction was quite obvious and was not observed in the sweep rates ranging from 10 mv/s to 200 mv/s. The characteristics of the peaks appearing at E_{pa} = 0.69V vs. SCE and E_{pc} = 0.23V vs. SCE. Both the peaks exhibit a diffusion controlled behaviour in the above sweep rate range. With a view to determining that the cathodic peak was not due to polypyrrole, cyclic voltammetric investigations were conducted with a 60 m*M* pyrrole in HCl medium. The electrochemical oxidation of pyrrole occurred at E_{pa} = 0.76V vs. SCE with no complementary cathodic peak up to 0V. The electrochemistry of pyrroles in aqueous medium was extensively investigated earlier[14,15] and features reported here suggested the irreversible oxidation of pyrrole. If the Fe(II) oxidation was catalysed in the presence of pyrrole, the anodic peak at E_{pa} = 0.45v

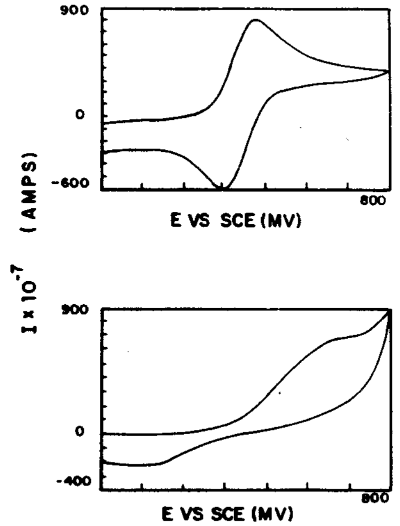

FIGURE 5 Cyclic voltammetric curves for 10 m*M* $FeCl_2$ in N HCl at a platinum wire working electrode ($A \approx 0.14$ cm^2). Reference electrode is a saturated calomel electrode. Bottom curve: current – voltage curve of 10 m*M* pyrrole. Sweep rate: 0.10 v/s.

should have been shifted in the negative direction. Possibly before Fe(II) is regenerated by electrocatalysis the experimental sweep has been completed. The positive potential shift observed here is indicative of a fast follow-up reaction with Fe(III) or Fe(II) itself in a possible complex state. The latter suggestion was discounted by spectrophotometric examination of Fe(II) and pyrrole in the time scale of an hour; there was no development of additional absorption peaks.

Spectrophotometric results

The UV-visible spectrum of the reaction mixture containing $FeCl_3$ and pyrrole is shown in Figure 6; this was recorded within five minutes of initiating the reaction. The peak at 333 nm appears to be characteristic of the Fe(III) species in HCl medium by a comparison with the spectrum of an authentic sample (charge transfer band). This peak disappeared within about 30 min. leaving the 450 nm peak and a broad absorption beginning beyond around 600 nm. Interestingly, the reaction mixture showed reappearance of the 330 nm peak after 24 hrs; perhaps this is caused by the air oxidation of the bound Fe(II) byproduct of the reaction to Fe(III). The laser interferometric features reported here refer to a solution of this composition.

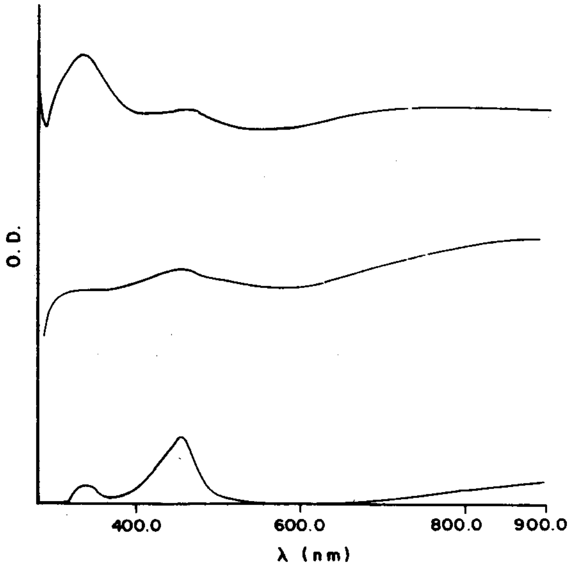

FIGURE 6 UV spectrum of the reaction between 0.1 M $FeCl_3$ and pyrrole. Solutions were taken at a) 5 mins, b) 30 mins, and c) after 11 hrs. The solution after 11 hrs was obtained by filtration of the precipitate.

CONCLUSIONS

The electrochemical oxidation of Fe(II) in HCl medium produces interesting laser interferometric fringe shifts in the presence of pyrrole. The fringe shift behaviour cannot be correlated to an electrocatalytic scheme. Further support for this conclusion has come from the cyclic voltammetric data where an Fe(II) and pyrrole mixture generated an irreversible redox couple with E_{pa} = 0.69V vs. SCE and E_{pc} = 0.23V vs. SCE. We propose that at the electrode/solution interface Fe(III) initiates the polymerization with the redox product Fe(II) being held by the polymeric species dispersed in solution. This species has a higher refractive index than $FeCl_2$.

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