

catalytic reaction is evaluated by monitoring one of the reaction products, H_2O_2 , either in bulk solution or at the concentric ring. The specific activity of the enzyme, glucose oxidase, has been evaluated as immobilized on a variety of surfaces. The relative contributions of mass transport and catalysis to the overall conversion rate has been determined by several independent methods.

Abstract No. 482**Characterization by Fluorescence Spectroscopy and Cyclic Voltammetry of Zinc Tetraphenylporphyrin Adsorbed onto Electrode Surfaces**

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Characterization of zinc tetraphenylporphyrin (ZnTPP) adsorbed onto electrode surfaces is being accomplished using luminescence and electrochemical experiments. Fluorescence spectra (both excitation and emission) of various forms of ZnTPP—crystalline, in solution and adsorbed onto a surface—have been obtained. Several surfaces have been studied as adsorption substrates, including glass, indium oxide coated glass, and basal plane pyrolytic graphite. Adsorption of the ZnTPP is accomplished either by applying a solution of ZnTPP in toluene onto the surface and allowing to dry, or by soaking the surface in the solution. Parallel cyclic voltammetric experiments have been carried out using ZnTPP adsorbed onto either In_2O_3 -coated glass or pyrolytic graphite as the working electrode.

Abstract No. 483**Interfacial Behavior of Carbon Supported Iron Phthalocyanine—A Laser Raman Spectroelectrochemical Study**

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The physicoelectrochemical properties of iron phthalocyanine, an analog of the biologically significant iron porphyrin, are of interest in electrocatalysis and other areas. The electrochemical behavior of iron phthalocyanine-on-carbon electrodes has been studied by cyclic voltammetry in 0.05N H_2SO_4 solution. Two reversible oxidation-reduction waves are observed in the region of 0 to -0.8 V vs. Hg/Hg_2SO_4 . Spectroscopic characterization, both *ex situ* and *in situ* at various applied potentials, have been carried out by Laser Raman Scattering. Results are presented.

Abstract No. 484**Catalytic Electroreduction of Molecular Oxygen Using Porphyrin Modified Electrodes**

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Catalytic electroreduction of molecular oxygen using iron- and cobalt-tetra-*o*-aminophenylporphyrins in the acidic media has been studied on unmodified and chemically modified glassy carbon electrodes. These results were compared with the previously described EC catalytic regeneration for iron tetra 4-N-methylpyridylporphyrin pentachloride. Decomposition of the yielded hydrogen peroxide to water and oxygen by the addition of the phthalocyanines as a catalase model was also studied in order to make oxygen reduction more efficiently.

Abstract No. 485**Electrochemical Studies on Mo-Fe Protein**

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The midpoint potentials and *n* values of Mo-Fe protein of azotobacter vinelandii (Av1) were determined by the coulometry at fixed potentials. The oxidation-reduction states of the Mo-Fe protein were discussed. The kinetics of reduction of Mo-Fe protein by the carrier (methyl viologen) is studied.

Abstract No. 486**A Spectroelectrochemical Method for Studying Redox Properties of Flavoenzymes**

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A new method has been developed which enables the quantitative reduction of enzymes. An electrochemical experiment, controlled potential electrolysis, is used to reduce a system containing an enzyme-mediator dye (methyl viologen) system in a modified spectrophotometric cuvet. Current transferred to the system is integrated; the progress of the reaction is monitored spectrophotometrically. This method was used in two types of experiment: (i) reductive titration (*n* measured), (ii) potentiometric titration ($E^{0'}$ measured). The method tested two well-characterized enzymes, flavodoxin and glucose oxidase, and on D-amino acid oxidase, previously uncharacterized.

Abstract No. 487**The Chronoamperometric Determination of Homogeneous Small Molecule-Redox Protein Reaction Rates**

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An essentially new application of chronoamperometry has been developed for the determination of homogeneous rates for the reactions between small molecule reductants and redox proteins. The chronoamperometric kinetics for the reactions of ferrous-EDTA with *C. vinosum* high potential iron-sulfur protein and horse cytochrome *c* were shown to be second order and compared well with stopped-flow kinetic results. The usefulness of this approach lies in the relative ease of working with powerful reducing agents and the small amount of protein required; it may prove to be particularly valuable in the study of multielectron transfer redox proteins and in those special cases where the redox centers are spectrally inaccessible.

Abstract No. 488**Electron Transfer Between Spinach Ferredoxin and Small Molecule Mediators**

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The reduction of spinach ferredoxin by $V(EDTA)^{2-}$, $Eu(DPTA)^{2-}$, and viologens has been investigated by various electrochemical methods such as chronoamperometry, pulse and differential pulse polarography, and rotating disk electrode. In chronoamperometry second-order conditions were used while in pulse, differential pulse, and R.D.E. technique, pseudo-first order conditions could be used. Rate parameters are as follows: $V(EDTA)^{2-}$, $k_{12} = 3.0 \times 10^4 M^{-1}S^{-1}$ (25°C, $\mu = 0.01M$, pH 5), $\Delta S^\ddagger = -21$ cal/mol-deg; $Eu(DPTA)^{2-}$, $k_{12} = 3.2 \times 10^5 M^{-1}S^{-1}$ (24°C, $\mu = 0.05M$, pH 7.3), $\Delta H = 9.88$ kcal/mol; trimethylene viologen cation radical, $k_{12} = 6.83 \times 10^4 M^{-1}S^{-1}$ (24°C, $\mu = 0.05M$, pH 7.3). These rates are consistent with Marcus Outersphere Theory. This work provides the first complete kinetic study of the reduction of such highly negative protein, and demonstrates the great advantage of electrochemical approaches to this problem.

Abstract No. 489**Electrochemical Studies of the Antitumor Antibiotics, Camptothecin and Bleomycin**

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The electrochemical properties of the antitumor antibiotics camptothecin and bleomycin have been studied by polarography and cyclic voltammetry. Model and modified compounds have been used to establish the electroactive moieties in the molecules. The relationships between the reversible reduction of camptothecin, the irreversible reduction of bleomycin, and the reversible reductions of several metalbleomycins are explored. Their significance for *in vitro* DNA crosslinking and *in vivo* antitumor action is discussed.

Abstract No. 490**Investigation of the Glutathion Dimerization Reaction in Deaerated Neutral Medium at a Platinum RDE**

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