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FUNDAMENTAL PROCESSES OCCURRING AT ELECTRODES.(U)
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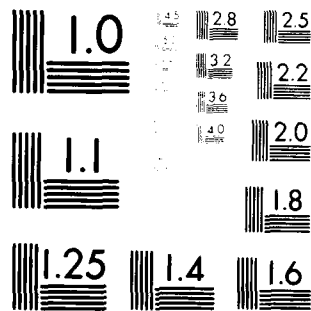
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The research program in electrochemistry reported here has concentrated on electrode kinetic studies at low ionic strengths, on methods for attaching molecules to electrode surfaces and on the electrochemical responses obtained from reactants confined to electrode surfaces. Brief summaries of the results obtained in each area are given.		

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Research Findings Resulting From This Grant

The ARO-supported research program in electrochemistry carried out in our laboratory during the last three years has focused on a variety of inter-related topics. The work has concentrated on electrode kinetic studies at low ionic strengths, on methods for attaching molecules to electrode surfaces and on the electrochemical responses obtained from reactants confined to electrode surfaces. Brief summaries of the results obtained in each area are given below.

Electrode Kinetics at Low Ionic Strength

This topic has received considerable attention in our laboratory for some time. The objectives were twofold: i) to establish if the diffuse layer could, in fact, be eliminated at charged electrode surfaces by suitable manipulation of the composition and concentration of electrolytes containing adsorbing anions (1); and ii) to account for serious discrepancies commonly observed between observed electrode reaction rates for simple reactants at low ionic strengths and the predictions of conventional double layer theory (2-6). We summarized our findings and conclusions in a recent paper (6). A germane portion of the Discussion Section of that paper ran as follows:

One is left with a clear dilemma in the form of electrocapillary data that show cations to be attracted into the interfacial region in electrolytes where electrode kinetic data imply that the reactant cation is repelled from the diffuse layer. This disagreement between the results of the two kinds of experiments seems too fundamental to yield to explanations based on proposed differences in planes of closest approach of reactant and supporting electrolyte ions or to the types of discreteness-of-charge effects that have been invoked to explain less glaring kinetic anomalies. The source of the discrepancy seems most likely to lie with the kinetic results. The observed behavior indicates that, although there is a net attraction of cations into the diffuse layer when anion adsorption exceeds the positive electronic charge on the

electrode, no corresponding enhancement in the rate of reaction of cationic reactants ensues. One might infer, therefore, that the site to which the cationic reactants must gain access before they can react retains a net positive potential even when the sum of the electronic and anionic charge on the electrode surface is negative. The kinetic data seem to show clearly that (at low to intermediate ionic strengths) specifically adsorbed anions do not effectively compensate for an equivalent quantity of positive electronic charge density on the electrode surface as viewed by cationic reactants at their reaction sites. Under these conditions the reactant appears to be able to differentiate between electronic and ionic charge on the electrode surface and to respond differently to each.

Electrochemical Responses from Attached Reactants

Improved electrochemical techniques were developed for observing current-potential responses from very small quantities of reactants anchored to electrode surfaces (7,8) and for measuring their rates of electron transfer in the adsorbed state (9).

Very little data are available on electrode kinetics exhibited by reactants which undergo simple charge transfer reactions while attached to electrode surfaces and one of our goals was to compare the electrochemical reactivities of selected reactants attached to electrode surfaces with the reactivities they display when freely diffusing in solution. A vital parameter in assessing the potency of redox catalysts attached to electrode surfaces is the rate at which they can be turned over, i.e., the rate at which the catalyst can be cycled between oxidation states by electron transfer from the electrode while it is catalyzing the oxidation or reduction of a substrate in solution. For example, several recent reports of the catalyzed reduction of oxygen at potential fuel cell cathodes have invoked such a cycle (10-14). With sufficiently large concentrations of substrate the catalyst

turn-over rate will be determined by the magnitude of the electron transfer rate constant for the attached catalyst. Thus, the evaluation of such first order rate constants for attached catalysts is essential in order to understand the factors that control catalyst activities. Efficient catalysts must have large electron transfer rate constants in the attached state so that a rapid measuring technique was required and developed (9).

Although a number of the systems investigated had charge transfer rates too high to measure, we were able to measure the charge transfer rate for 9,10-phenanthrenequinone in the attached state. Of particular interest was the determination of the temperature dependence of the rate constant because such measurements offer insight into the factors that set the upper limit on rates of electron transfer with attached reactants. The magnitude of this limiting rate will determine the ultimate activities obtainable with catalysts anchored to electrode surfaces. The results of these experiments provided an estimate of the appropriate pre-exponential term in the rate law for attached reactants and a formalism was worked out (9) by which the reactivities of attached and unattached reactant could be compared. Among the tasks remaining is the quantitative testing of the formalism with a greater variety of experimental data.

New Schemes for Attaching Reactants to Electrodes

We have devoted considerable effort in the past three years to the development of surface chemistry that can be exploited to bond reactants to electrode surfaces (7, 15-21). Some of this work has been supported under other auspices and some by ARO. One of the most potent attachment schemes involves the use of relatively high molecular weight polymeric ligands that are strongly adsorbed on graphite surfaces where they serve as binding sites for metal complexes. We have investigated poly(4-vinylpyridine) most extensively and found it to be particularly effective in the binding of

specific metal complexes that show a high affinity for pyridine ligands (19,21). Quite recently we have observed that the same polymer can be used to bind a wider variety of molecules by means of a much more general electrostatic type of binding (22). This observation appears to have considerable potential for extension and elaboration.

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Reactant Adsorption in Differential Pulse Polarography. Effects of Adsorptive Depletion of Reactant, Non-linear Adsorption Isotherms and Uncompensated Resistance

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Effects of Reactant and Product Adsorption in Normal Pulse Polarography

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Electron Transfer Kinetics with Both Reactant and Product Attached to the Electrode Surface

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Facile Attachment of Transition Metal Complexes to Graphite Electrodes Coated with Polymeric Ligands. Observation and Control of Metal-Ligand Coordination Among Reactants Confined to Electrode Surfaces

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Spontaneous Coating of Graphite Electrodes by Amino Ferrocenes

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Electrostatic Binding of Metal Complexes to Electrode Surfaces Coated With Highly Charged Polymeric Films

Noboru Oyama and Fred C. Anson
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Evaluation of Rate Constants for Redox Self-Exchange Reactions from
Electrochemical Measurements with Rotating Disk Electrodes Coated with
Polyelectrolytes

Kiyotaka Shigehara and Fred C. Anson
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