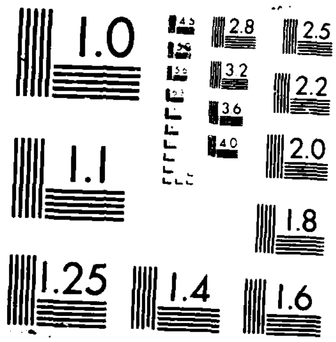
AD-A186 156 FUNDAMENTAL STUDIES OF SURFACES PROCESSES AND TRACE ANALYSIS USING SOLID (U) STATE UNIV OF NEW YORK AT BUFFALO DEPT OF CHEMISTRY S BRUCKENSTEIN 10 AUG 87 1/1

UNCLASSIFIED AFOSR-TR-87-1027 $AFOSR-83-0004 F/G 7/4 NL



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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR-TR- 87-1027	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) FUNDAMENTAL STUDIES OF SURFACES PROCESSES AND TRACE ANALYSIS USING SOLID ELECTRODES		5. TYPE OF REPORT & PERIOD COVERED FINAL TECHNICAL REPORT 1 Oct 1983 - 31 Dec 1986
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) STANLEY BRUCKENSTEIN		8. CONTRACT OR GRANT NUMBER(s) AFOSR 830004
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry, State University of New York at Buffalo, Buffalo, NY 14214		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F 2303 A1
11. CONTROLLING OFFICE NAME AND ADDRESS Air Force Office of Scientific Research, Building 410, Bolling AFB, D.C. 20332 NC		12. REPORT DATE 10 August 1987
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Same as 11		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED.

DTIC SELECTED OCT 0 6 1987 S D

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

Approved for Public Release; Distribution Unlimited

CE

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

ELECTRODE KINETICS, SOLID ELECTRODES, GAS POROUS ELECTRODES, HYDRODYNAMIC VOLTAMMETRY, QURTZ CYRSTAL MICROBALANCE, CARBON DIOXIDE, SULFUR DIOXIDE, PHENOLS, ALLYL ALCOHOL, FLOW INJECTION ANALYSIS, KUOTECKY-LEVICH METHOD.CONDUCTOMETRY, SENSORS, AMPEROMETRY, UNCOMPENSATED OHMIC RESISTANCE

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The objective of the work carried out under this grant was to perform physical electrochemical and electroanalytical studies at various kinds of solid electrodes. The physical electrochemical investigations were divided into studies of heterogeneous electrode kinetics, underpotential deposition and electrocatalysis. The electroanalytical work areas involved trace analysis of solutions using hydrodynamic voltammetry and of solutions and gases using porous electrode structures.

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Key accomplishments in the physical electrochemistry area comprised a) determining the mechanism of the catalysis of formic acid electrooxidation by underpotentially deposited species, b) modelling the interaction of mass transport and light intensity in photoelectrochemical cells and testing the model, c) determining how the reduction of strong and weak acids is affected by the simultaneous reduction of water, and thereby obtaining the explanation for well-known discrepancies in rate constants for weak acid dissociation rates by the Koutecky-Levich method, d) and demonstrating the value of the in situ use of the quartz crystal microbalance, QCM, in electrode kinetic studies. The utility of the QCM technique was illustrated determining the mechanism by which the first monolayer of oxide ions is inserted into a gold surface, determining the underpotential adsorption isotherms for lead and silver on gold in acetonitrile and weighing a Langmuir-Blodgett monolayer film.

Novel porous electrode techniques were developed for the analysis of trace species present in both liquid and gas phases. A miniature gas phase sensor for concentrations of carbon dioxide at ambient and higher levels were developed, as was a sensor for parts per billion levels of sulfur dioxide. Porous electrode-based sensors for flow injection analysis were developed and applied in four different ways to the analysis of volatile and nonvolatile species dissolved in the flowing stream. Techniques were demonstrated for volatile, nonelectroactive species. Sensitivities at the nanogram level were demonstrated.

Two novel and simple electronic circuits were developed for electrochemical applications. One was a high precision means for real-time uncompensated ohmic potential drop correction. This technique is completely automatic and requires no operator intervention. The other was a extremely simple circuit for intraconversion between potentiostatic and galvanostatic control does not require opening the feedback loop of the potentiostat. Both circuits can be added externally to an existing commercial potentiostat. They permit exercising close control of working electrodes subjected to complex current/potential control sequences required in non-routine physical and electro- analytical studies.

AFOSR-TR- 87-1027

FUNDAMENTAL STUDIES OF SURFACE PROCESSES AND TRACE ANALYSIS USING SOLID ELECTRODES

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10 August 1987

Final Technical Report For the Period 1 October 1983 - 31 December 1986

GRANT NUMBER AFOSR 83-0004

Prepared for
United States Air Force Office of Scientific Research
Building 410
Bolling AFB, DC 20332

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RESEARCH COMPLETED UNDER AFOSR SPONSORSHIP

The research undertaken and completed under this grant fell into the areas of electrochemistry and electroanalytical chemistry. The completed studies have been categorized below under the headings, Physical Electrochemistry, Crystal Microbalance Studies, Amperometric Porous Electrodes Studies, Conductometric Porous Electrode Studies, Electroanalytical Chemistry and Electrochemical Instrumentation, and is discussed below under these headings.

Physical Electrochemical Studies.

Mechanism of Electrocatalysis of Formic Acid Oxidation. (23). The catalysis and inhibition of formic acid electro-oxidation that may accompany metal-submonolayer formation on polycrystalline platinum was studied quantitatively using the rotating ring-disk electrode (RRDE) technique. Under controlled flux conditions one can attain limiting current behavior for the oxidation of formic acid and thereby determine the upper limit for the optimum adatom coverage for lead and bismuth. These values are found to be 30-35% of the real area of the platinum electrode. The electro-oxidation experiments in this paper are correlated with the literature dealing with polycrystalline and single-crystal studies of hydrogen adsorption and formic acid oxidation at platinum to explain differences of the behavior of various underpotential deposited (UPD) species. The poisoning of the electro-oxidation process of formic acid requires the presence of adsorbed hydrogen or unhindered access to the first adsorbed intermediate COOH that was produced. During the initial stages of UPD, submonolayers of silver or copper do not deposit significantly on Pt(100), the plane that was responsible for most of the electro-oxidation of formic acid. Therefore, UPD silver or copper cannot inhibit poisoning of the formic acid oxidation process by decreasing hydrogen adsorption, or restricting access to COOH via a third body mechanism. Bismuth, lead, and other UPD species with radii larger than platinum do deposit significantly on Pt(100) at low UPD coverages, and can therefore slow the poisoning of the formic acid process on this plane.

Kinetic Study Hydrogen Ion Limiting Currents In The Presence of Water Reduction. (1), (24), (25). The simultaneous mass-transport controlled reduction of hydrogen ions and charge-transfer controlled reduction of water was studied in 1 M KCl solutions of dilute strong acid. Using the sinusoidal hydrodynamic modulation techniques, SHM, at a rotating disk electrode, RDE, these studies confirm the existence of a thin reaction layer at the electrode surface where the neutralization reaction between H^+ and OH^- produced from water reduction causes a decrease in the limiting flux of hydrogen ions at the electrode. An approximate solution to the convective--diffusion problem was obtained, as was the decrease in modulation current response and the thickness of the reactiou boundary layer, w_r. The negligible distortion in the conventional convective-diffusion limiting RDE current accompanying the parallel processes is explained by the magnitude of w_r. Separability of the mass-transfer and non-mass transfer controlled components by the SHM method is demonstrated with studies at various applied potentials, modulation amplitudes and frequencies. ˘ ır studies were undertaken with weak acids and the origin of the sloping limiting-current r explained. Corrections to the Kuotecky-Levich analysis were given.

Effect of Mass Transport on Photoelectrochemical Cells. (6). Our object was to describe the kinetics of semiconductor-based photoelectrochemical cells in terms of rigorously specified light and mass transport fluxes. In general, choosing the latter two experimentally controllable variables provides practical tests. The theory treats the total voltage applied across the semiconductor/solution interface as the sum of the voltage drop across the semiconductor and the potential associated with the electrochemical process. In particular, choosing the individually well-understood pair of elements (p-n Si, Hg dissolution) allowed us to test two aspects of the theory. One aspect requires an a priori model of both the semiconductor and electrochemical current-voltage responses. The second, more general approach describes the response in terms of the individual impedances of the semiconductor and electrochemical cell, and requires no detailed mechanistic knowledge. Agreement between experiment and theory for both approaches was excellent.

Infrared Studies of Polyazulene. (9). Electrochemically formed homo-polyazulene and mixed polyazulene-polypyrrole films have been studied by infrared spectroscopy. Infrared spectra are consistent with a polymerization mechanism that involves loss of hydrogen atoms and produces an amorphous polymer structure. The spectral differences between the oxidized (conducting) and reduced (non-conducting) forms of polyazulene show the presence of a polarization interaction in the oxidized polymer, even though the structure of both forms was similar. The i.r. bands of anions are present only for the oxidized form of the polymer, a result that indicates the existence of cationic charge centers on the polymer backbone. The counter anions have no detectable effect on the polymer structure and only a small effect on certain vibrational bands of the oxidized form. The electrochemical preparation of a mixed polyazulene-polypyrrole phase was discussed and the mixed phase was found by i.r. spectroscopy to be a random copolymer. A bilayer polymer structure consisting of polyazulene and polypyrrole was also prepared and the i.r. spectra of this polymer structure did not indicate any interfacial interactions.

Interactions Between Thiourea and Silver Metal. (18). In alkaline solutions, when the potential of the silver electrode was more positive than - 450 mV vs. sce, thiourea undergoes decomposition and a sparingly soluble silver sulfide film forms as a product of the accompanying anodic reaction. These processes are controlled by convective diffusion and depend upon the thiourea concentration. During the reverse cathodic scan, two cathodic stripping peaks are observed. The first one corresponds to the stripping of Ag_2S (bulk) and the second one to the stripping of an adsorbed layer of Ag_2S. *Hydrosulfide ions* (HS^-) *are produced by these two cathodic reactions.* The formation of an adsorbed layer of Ag_2S was confirmed in rotating ring-disk electrode experiments.

Quartz Crystal Microbalance Studies.

Instrument. (8). TTL-based circuitry was described for measuring the resonant frequency of an oscillating quartz crystal having one face in contact with an electrolytic solution. The circuitry facilitates application of the quartz crystal microbalance technique to in situ electrogravimetric studies of submonolayer and many monolayer thick electrodeposited and electrosorbed films. The effect of solution temperature and viscosity, and height of liquid above the crystal were investigated and the results correlated with theory. An in situ solution method for determining the mass sensitivity of the crystal was described and the latter sensitivity was shown to be the same as the calculated vacuum sensitivity. The effect of double layer structure and specific adsorption was discussed.

Mechanism of Monolayer Oxide Formation at Gold. (7). The mechanism for the formation of the first monolayer of electrosorbed oxygen at a gold electrode was shown to proceed via the three step reaction sequence: (1) $Au\text{-}(H_2O)_{ads} = Au\text{-}OH + H^+ + e^-$; (2) $Au\text{-}OH = Au{=}O + H^+ + e^-$; and *finally the place exchange reaction* (3) $Au{=}O + H_2O = O{=}Au\text{-}(H_2O)_{ads}$ in which a water molecule adsorbs on the gold atom. The mechanism was established by determining the in situ change in weight of the gold electrode concomitantly with the cyclic voltammogram using the oscillating quartz crystal method.

UPD Studies in Acetonitrile. (5). The underpotential deposition of lead and silver on gold was studied in acetonitrile as a solvent. The rotating disk electrode, the rotating ring disk electrode and the quartz crystal microbalance techniques were used. Satisfactory agreement for the coverage values as a function of underpotential were obtained among the rotating electrode and the quartz crystal balance methods. The quartz crystal microbalance method is more general that the rotating electrode methods since the species being studied need not be electroactive.

Langmuir-Blodgett Films. (11). The quartz crystal microbalance was used to follow the deposition of mono- and multilayer Langmuir-Blodgett films of calcium stearate on gold. The change in frequency of the oscillating quartz transducer was a linear function of the number of layers deposited. The weight associated with each deposited layer agrees within 25% of that calculated from the reported molecular surface area.

Amperometric Porous Electrode Studies.

Stripping Analysis of Trace Gas Phase Species. (3). Gaseous H_2S was accumulated on the surface of a porous silver membrane electrode at constant potential and directly determined by cathodic stripping voltammetry. The sensitivity of the method, expressed by the slope of the regression line for the dependence of the stripping peak current on the amount of H_2S in the gas sample, is 357 mg of H_2S/mA. The reproducibility of the determination expressed in terms of the relative standard deviation was 3.2%. Phenomena observed during cathodic polarization of the silver porous membrane electrode, either clean or covered with deposited Ag_2S, are briefly discussed and the resultant conditions for optimal analysis are given.

Determination of Cyanide by Pneumatoamperometry. (10). A rapid pneumatoamperometric method for quantifying cyanide in the presence or absence was described. The gaseous mixture of hydrogen cyanide and hydrogen sulfide was separated by inserting a short chromatographic column packed with silica gel between the reaction vessel used to generate the volatile acids and the porous gold electrode that detects them. The detection limit was ca. 5 ng cyanide in 2 ml of solution regardless of sulfide content. The detection limit for sulfide was ca. 1.0 ng in 2 ml of solution when cyanide was present and ca. 0.7 ng in absence of cyanide. Both sulfite and nitrite interfere.

Porous Electrode Detector For Flowing Liquids. Solid electrodes used in voltammetric flow--through detectors are subject to passivation and gradual loss of sensitivity due to electrode surface contamination by dissolved species or electrode reaction products. A successful approach that avoids problems associated with electrode fouling even under very unfavorable matrix conditions is to use a metalized gas porous membrane electrode (GMPE). Such a metalized GMPE functions as a gas diffusion electrode. It permits selective detection of soluble, volatile species that reach the unmetalized, hydrophobic side of the membrane. In the procedure we have exploited, a solution was impinged on the unmetalized face of the GPME. Volatile species in the solution partition directly into the membrane's pores and diffuse to the metalized face where they are electrolyzed. This geometry produced a sensitive flow-through detector that we used for flow injection analysis. This differs from the conventional pneumatoamperometric technique in which a solution containing the volatile, electroactive species is purged with a nonelectroactive gas and the gas stream was impinged on the unmetalized side of the membrane. Four different methodologies based on this principal have been demonstrated.

Detection of Volatile Electroactive Species. (12). The gas porous electrode structure that detects volatile electroactive species in a flowing liquid stream described in the previous paragraph was evaluated for its utility in flow injection analysis. The electrode was fabricated by depositing a porous gold layer on one side of a porous Teflon membrane. The gold serves as the amperometric electrode which consumes dissolved, volatile species that was transported from the flowing solution through the membranes to the metalized face where it was electrolyzed. Nitrite ion was determined by reaction in the carrier stream to produce nitric oxide and iodine, and both are electrooxidized at the gold electrode. The detection limit was 30 pg of nitrite ion. Dissolved, nonvolatile electroactive species do not interfere.

Detection of Nonvolatile Species by Reaction with Bromine. (13). Phenols and other important class of compounds in industrial and environmental analysis, are known for their tendency to polymerize upon anodic oxidation and thus form insulating films on the electrode. Well-defined voltammetric responses are usually obtainable only at very low phenol concentrations. The situation has been advantageously exploited by numerous liquid chromatography methods that employ direct amperometric detection of phenols. However, electrode fouling occurs in several chromatographic studies when the injected samples contained more than 200 ng of a phenol. A successful approach that avoids problems associated with electrode fouling even under very unfavorable matrix conditions is to use a metalized gas porous membrane electrode (GMPE) in conjunction with the bromination method for phenol determination. Bromine was added to the phenol-containing stream, and excess unreacted, bromine diffused through the porous membrane to a platinum electrode where it was detected. Linear calibration curves were obtained in the range 20- ca. 300 ng for the model compounds, phenol, resorcinol and 2-naphthol.

Detection of Nonelectroactive, Volatile Species Using a Redox Mediator. (14). In this technique we determine a volatile, nonelectroactive species, Z, after it diffuses through a porous membrane into the detection cell. In one realization of this method, Z reacts with the oxidized component, Ox, of a redox couple in contact with the a porous electrode to form Red and electroinactive products, P. By use of the appropriate electrode potential, Red is oxidized back to Ox at the electrode surface. The current required for this redox process becomes a direct measure of the concentration of the volatile species.

The Ox/Red redox couple acts as mediator in the determination of Z. Its concentration and solution environment can be optimized for the chemical and electrochemical steps because the electrochemical cell was isolated from the carrier stream by the hydrophobic gas porous membrane. The Os(VIII)/OS(VI) redox couple in alkaline media reacts rapidly with a number of organic compounds and has excellent redox behavior. For this reason, we used it to validate this approach by using it as mediator in the determination of acetone, methanol, and ethanol. Nanogram sensitivity limits are feasible with this method, the limitation being the rate of reaction with Os(VIII) and the analyte's volatility.

Double Porous Electrode Membrane Detector. (19). A novel dual electrode detector capable of being used in flowing streams was described. One electrode generates a volatile reagent from a constituent present in the flowing stream which then reacts with a dissolved analyte also present in the flowing stream. Excess volatile reagent diffuses through a non-wetting porous membrane to a second electrode at which the unreacted volatile reagent was determined by constant potential electrolysis. The utility of this detector was demonstrated by the determination of allyl alcohol with electrogenerated bromine in the range 23 - 697 ng of allyl alcohol. This configuration avoids the problems associated with adding very reactive reagents to the flowing stream. For example, in the case of adding bromine, highly inert plumbing must be used to prevent reaction with the bromine. Also, electrogeneration of the reagent allows exquisite control of the amount of excess that will permeate the membrane and be detected. The latter feature greatly simplifies determining widely differing concentrations of dissolved, nonvolatile species in the flowing stream.

Conductometric Porous Electrode Studies.

Porous and permeable membrane electrode structures are now widely exploited in sensors for species in aqueous and gas phases. Potentiometry and amperometry are now regularly applied in conjunction with membrane electrode methodology. Only recently has the classic technique of conductometry been used in tandem with membrane electrodes. We have be instrumental in *developing sulphur dioxide and carbon dioxide conductance sensors based on structures involving* porous membranes and thin water layers. Two novel detector are described and the principles governing their response are discussed below.

Miniature Continuous Conductometric Sensor for Carbon Dioxide.

A miniature and continuous conductometric sensor was described for the determination of carbon dioxide in the atmosphere and in nonacidic and nonbasic gases. Gaseous carbon dioxide diffused through a hydrophobic, gas-porous membrane into a thin layer of pure water. The back wall of the thin water layer was a porous screen that separated the water layer from a mixed--bed ion exchanger column. The ion exchanger continuously removed ionic species from the water layer including the products from the dissociation of CO_2(aq). Conductivity electrodes positioned in the thin water layer measure its conductance. The diffusion of carbon dioxide through the membrane into the thin water layer and the removal of ionic species through the screen by the mixed-bed ion exchanger established a steady-state concentration gradient of CO_2. This gradient was proportional to the partial pressure of CO_2 in the gas phase, and cell conductance was proportional to $P_{CO_2}^{1/2}$. This device was evaluated for use in the determination of carbon dioxide levels up to 1% and conformed to the theoretical predictions.

Sulfur Dioxide Sensor. (16). A conductometric sensor for the determination of atmosphere sulfur dioxide levels was described. It consisted of a hydrophobic, gas-porous membrane that separated the gas sample from a thin film of pure water. Sulfur dioxide from the gas phase diffused through the membrane and rapidly equilibrated in the water layer. Conductivity electrodes positioned within the thin layer measured its conductance. The theory relating the square of the equilibrium conductance to the partial pressure of sulfur dioxide was given. The behavior of the sensor to sulfur dioxide was characterized and contrasted to that of carbon dioxide. Linear calibration curves were obtained over a range of 20-1000 ppb SO_2. Response times were on the order of 90-120 s.

Electroanalytical Studies.

Lead as an Electrode Material. (2). The behavior of lead as an electrode material for electroanalytical purposes was studied in 1.0M sulfuric acid. The useful negative range of potential was approximately -0.57 to -1.20 V vs. SCE for conventional voltammetry at a rotating disk electrode. For the sinusoidal hydrodynamic modulation technique, the negative limit was about -1.25 V. Studies of the reduction of cadmium ion, thallium(I) ion, and p-nitroaniline showed that the behavior of a rotating lead-disk electrode was comparable to that expected on the basis of theory. Limits of detection were in the micromolar range.

Rugosity Effects at Rotating Electrodes. (4). In this research group as well as others substantial emphasis has been placed on the surface preparation of rotating disk electrodes, RDE's. In the literature, there was the widespread belief that very highly polished electrodes would be required to obtain Levich behavior. A study was undertaken to determine the largest abrasive size that could be used to polish the surface of a RDE without producing a significant deviation from the Levich response (4). This information will allow the most rapid preparation of the surface of a RDE. In fact, the only requirement is that the rugosity of the polished electrode be an order of magnitude smaller that the Levich diffusion layer thickness. This was shown in our study where we demonstrated that polishing a gold or platinum disk with 5 micron abrasive results in the same limiting currents as polishing the same electrode with abrasives as small as 0.05 micron, provided the rotation rate does not exceed 10,000 rpm.

Micro Ring Electrodes. (22). A very thin ring electrode (VTRE) inlaid in an insulating glass plane was been fabricated and studied. The purpose of this geometry was to increase the current density and attain a higher analytical sensitivity and make possible the determination of faster heterogenous and homogeneous rate constants. Our electrode's inner radius was 4 mm and its width was 0.7 micron. The current-potential and current-time behavior for the reduction of ferricyanide in potassium chloride and iodine in excess iodide were studied at the rotating and the stationary very thin ring electrode. Comparison of the electrochemical data with theory indicated that the ring electrode was approximately 0.3 micrometer below the surface of the insulating plane. This conclusion was verified by means of scanning electron microscopy. A fifteen fold increase in current density as compared to the RDE was attained, and a modelling of the recessed electrode geometry permitted the direct measurement of the rate constant for ferricyanide reduction to ferrocyanide ion.

Electrochemical Instrumentation.

Circuit for Closed Loop Conversion Between Galvanostatic and Potentiostatic Modes. Frequently in electrochemical studies it is required to control the potential (current) at an electrode and then switch to current (potential) control. The crude technique of disconnecting the cell from the potentiostat (galvanostat) and reconfiguring the setup is hardly ever justifiable in careful studies. The latter procedure causes the working electrode to experience unknown potential transients. However, it is done in practice because the existence of other alternatives is unfamiliar to most workers. Note that commercial instruments that have a switch that performs this operation accomplish this intraconverision by a procedure that opens the feedback loop of the electronics. A circuit for accomplishing this intraconversion without open the feedback loop of a potentiostat appeared in the literature (S. Bruckenstein and B. Miller, J. Electrochem. Soc. 117, 1970, 1032) and was patented (U.S. Patent No. 3,918,005). This patent is assigned to ATT&T Bell Laboratories. We have devised a much simpler and faster responding circuit to accomplish the same goal. It can be added to any existing commercial potentiostat and the speed of intraconversion between potential control and current control is solely determined by the response of the potentiostat. A patent disclosure is being filed that describes this circuit.

Circuit for Real Time Uncompensated Ohmic Potential Drop Correction. We have devised circuitry that can be added externally to any existing commercial potentiostat that permits real time correction of ohmic potential drops. The principal involved does not required any prior knowledge of the IR drop, or manual or computer adjustment of circuit components. A patent disclosure is being filed that describes this circuit. It has been tested on three electrochemical systems, the reduction of ferrocyanide ion to ferrocyanide ion, the reduction of silver ion to silver metal, and the oxidation of iodide ion to iodine. The least squares slope of the theoretical logarithmic plot was used as a criteria of successful performance. Slopes, after IR correction were within one standard deviation of the theory, 0.2 to 0.3 mV. No other published circuit has ever demonstrated such accuracy and precision. Corrections for uncompensated ohmic potential drop were on the order of 50 mV in these studies. The instrument has demonstrated the ability to correct up to 1000 mV using dummy cells.

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All reference a given in the next section, **PUBLICATIONS RESULTING FROM AFOSR SPONSORSHIP.**

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PERSONNEL

The following individuals were supported on this grant.

Ph.D. Students.

Degrees Received. Robert. F. Mack; John. W. Sharkey; James S. Symanski, Randy v. Smith, Mark Malczewski.

Degrees In Progress. Nancy Adinolfe, Michael Shay.

M.S. Students.

Degrees Received. June Y. Yip; Hieu Ngyuen.

Senior Collaborators.

Postdoctorals. Mani Shabrang, Sundarajan Swathirajan, Franticek Opekar, Antonin Trojanek;

Visiting Faculty. Dr. Maria Hepel, Associate Professor of Chemistry, State University College, Potsdam, NY; Dr. Tadeusz Hepel, Assistant Professor of Chemistry, Clarkson University, Potsdam, NY.

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