THE FABRICATION AND CHARACTERIZATION OF SURFACE-
FUNCTIONALIZED MICROSTRUCTURES: MONOLAYERS AS PRECURSORS TO
MOLECULAR WIRES

by

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B.S., The Ohio State University
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ABSTRACT

Chapter 1

An introduction to the field of self-assembled
monolayers is given. Orthogonal self-assembly of monolayers
is described. A future intersection between monolayer
technology and molecular device technology is suggested.
Molecular wires, single molecules attached covalently between
very small-gap pairs of microelectrodes, are introduced and
discussed.

Chapter 2

A new microfabrication lift-off process for the micron-
scale patterning of indium tin oxide (ITO) microelectrode
arrays is reported. Conductive indium tin oxide can easily be
patterned on the micron scale with an electron beam
evaporation lift-off process if a conductivity-enhancing Au
layer is deposited between two ITO layers. The
electrochemical behavior of e-beam deposited ITO/Au/ITO is
characterized and compared to single ITO layers. Examples of
microelectrode array designs optimized for particular types
of experiments are given.

Chapter 3

Substituted carboxylic acids selectively form self-
assembled monolayers on ITO. ITO macro- and microelectrodes
exposed to a dilute ($10^{-3}$ M) solution of alkylferrocene
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1:1 ethanol/hexane are derivatized while an Si$_3$N$_4$ substrate
is not. Electrochemical characterization of ITO
microelectrode arrays indicates that the alkylferrocene
carboxylic acid molecules derivatize the surface with
monolayer coverage. Analysis by Auger electron spectroscopy
confirms the presence of a fluorine-containing carboxylic
acid molecule on ITO surfaces and its absence on the Si₃N₄. The effects of various plasma cleaning treatments on monolayer formation by carboxylic acids on ITO is examined, and it is found that an Ar/H₂ plasma cleaning sequence is optimal.

Chapter 4

Simultaneous, independent, electroactive monolayer formation by thiols on Au and either carboxylic acids or phosphonic acids on ITO surfaces, all present in the same solution, is demonstrated. Characterization by cyclic voltammetry, Auger electron spectroscopy (AES), and secondary ion mass spectrometry (SIMS) confirms that the thiol monolayers form exclusively on the exposed Au and the acids chemisorb exclusively to the ITO. This kind of system may eventually be useful for making molecular wires, single molecules oriented and attached between very small pairs of electrodes.

Chapter 5

The diffusion of Ag⁺ ion in the solid, frozen electrolyte medium HClO₄ · 5.5 H₂O was studied by measuring transit times between band electrodes of known dimension. The transit times measured at each temperature fell into multiple time regimes, indicating that at least two distinct phases exist in the solid over the temperature range -45 to -85 °C, with each phase on a size scale larger than the thirty micron microelectrode array. The activation energy for diffusion of Ag⁺ ion in each phase of the two phase case is reported.

Thesis Supervisor: Mark S. Wrighton

Title: Provost and CIBA-GEIGY Professor of Chemistry
"A 2-iron beats a 3-wood every time."

C.D.D., Sr.
1944-1992
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Now on to something new. I'll miss you all.
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Chapter 1

Introduction
In the last decade, self-assembled monolayers (SAMs) have come from relative obscurity to become a widely used method of surface modification.\textsuperscript{1} The self-assembled monolayers discussed here are a means of surface modification in which a single layer of molecules spontaneously chemisorbs in a more or less ordered way onto a surface from a solution containing the adsorbate molecule, L, Scheme 1.I. Work that began as an odd report by Bigelow, Pickett, and Zisman in 1946\textsuperscript{2} gained more notice in 1984 when Sagiv and Moaz\textsuperscript{3} published a comparison between SAMs and monolayer films deposited by the Langmuir-Blodgett technique. This delay was probably related to the need for good analytical tools to detect and characterize monolayers.

X-ray photo electron spectroscopy (XPS), Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS), and reflectance FTIR spectroscopy are a few of the analytical instruments whose appearance made systematic study of monolayers easier.\textsuperscript{4} Recently, scanning tunneling microscopy (STM) and atomic force microscopy (AFM) have shown some promise as ways to characterize monolayers.\textsuperscript{5} Now, in addition to being an effective and useful method of surface modification practiced by a large number of researchers,\textsuperscript{1} the technology of SAMs is often quickly applied to the newest areas of research, such as C60 chemistry.\textsuperscript{6} The true fulfillment of monolayer technology, however, probably lies somewhere in the future.
**Scheme 1.I.** The spontaneous, selective formation of a monolayer by molecule L on an Au microelectrode on a Si$_3$N$_4$ substrate, shown in cross section. Selectivity refers to the lack of monolayer formation on the Si$_3$N$_4$ substrate.
This thesis, through its exploration of the orthogonal self-assembly of monolayers, is meant to make a ground-floor contribution toward using monolayer techniques to create useful, molecular-scale devices. Orthogonal self-assembly (OSA) of monolayers occurs when two materials, Au and ITO in this work, are exposed to a solution containing two ligands, each with a different functional group, \( L_1 = \text{thiol} \) and \( L_2 = \text{carboxylic acid or phosphonic acid} \), and one ligand selectively derivatizes only one material while the other ligand selectively derivatizes only the other material, Scheme 1.II. Two such systems have been examined previously in this research group: thiol and carboxylic acid terminated molecules adsorbed to Au and Al\(_2\)O\(_3\), respectively,\(^7\) and isonitrile and disulfide terminated molecules adsorbed to Pt and Au, respectively.\(^8\) Both of those systems have important limitations mentioned later in this chapter.

Molecular device technology, i.e. having a single molecule function as some kind of device, is one possible destination of the semiconductor industry's drive to more powerful computers through smaller size and greater device density. Currently, this trend is being pursued by the further refinement of conventional lithographic techniques and solid-state semiconductor devices. Moore's law, the doubling of the number of transistors in an integrated
Scheme 1.II. Orthogonal self-assembly (OSA) of molecules $L_1$ and $L_2$ onto electrodes made of Au and ITO. OSA is demonstrated when only pure monolayers of $L_1$ or $L_2$ are formed on their complimentary materials, and neither $L_1$ nor $L_2$ adsorb to the substrate.
circuit every 18 months, has been followed rigorously for 30 years,\(^9\) to the point that a current (1993) microprocessor such as the Intel Pentium\(^{\text{TM}}\) has millions of transistors on each chip. Soon, manufacturers will be compelled to move from UV lithography to x-ray and electron beam lithography\(^{10}\) to downsize competitively. At that time, the small size of fabricated features will make it realistic to consider production of molecule-based devices by combining microfabrication with self-assembled monolayer technology.

Some monolayer-based devices have already been made for sensing\(^{11}\) and rudimentary molecular recognition.\(^{12}\) Another promising, if slightly more complex, application of self-assembly is the concept of making "molecular wires" which could be strung between molecule-scale pairs of electrodes, Scheme 1.III. Although practically pre-nascent, the progress in this area of research has been examined recently.\(^{13}\) Balazs et al. have theorized about how molecules might interact with the electrode structures,\(^{14}\) and Hopfield et al. have proposed memory devices based on molecular wires.\(^{15}\)

The type of assembly in Scheme 1.III mandates research in three areas before it can be realized: the small gap structure, the bridging molecule, and the method of attachment.

The structure will need to have an inter-electrode spacing the same size as a bridging molecule of interest, a
**Scheme 1.III.** A cross-sectional view of a molecule self-assembled between two electrodes of dissimilar materials. The molecule is a donor (D) - chromophore (M) - acceptor (A) ensemble capable of separating charge by intramolecular electron transfer. Terminal functional groups $X_1$ and $X_2$ attach the molecule to the structure. $X_1$ interacts only with $M_1$, and $X_2$ interacts only with $M_2$, thus orienting the molecule in the gap.
span of at most a few hundred angstroms. X-ray and electron beam lithography,\textsuperscript{10} perhaps in combination with a technique like shadowing,\textsuperscript{16} will likely make it possible to fabricate this kind of microelectrode array.

Two kinds of molecules which would be of interest for examination as molecular wires are shown in Scheme 1.IV. Conjugated soluble rigid-rod polymers, already the subject of monolayer research,\textsuperscript{17} would allow study of conduction along the backbones of the molecules with the minimization of the chain-to-chain hopping mechanism which dominates in conventional conducting polymers. The molecule at the bottom of scheme 1.IV is an imaginary assembly of molecular parts under active study in the Wrighton group.\textsuperscript{18} Other researchers are engaged in the study of similar molecules capable of intramolecular electron transfer.\textsuperscript{19} The premise for these studies is that an ensemble of donor–chromophore–acceptor molecules oriented as a molecular wire would be capable of separating charge when exposed to light, functioning as a molecular photovoltaic. Furthermore, modeling of electron transfer processes like those that occur in photosynthesis\textsuperscript{20} might be done more effectively by placing molecules in a molecular wire configuration.

The third aspect of the molecular wire assembly, and the subject of this thesis, is the method of attaching the molecule. True orthogonal self-assembly of functional groups at the ends of the bridging molecule would be capable of performing this minuscule yet mighty task.
Conjugated Rigid Rod

\[ \text{HOOC}(\text{CH}_2)_n \text{C}_6\text{H}_5 \text{Cl} \left( \begin{array}{c} \text{OR} \\ \text{OR'} \\ \text{OCH}_3 \end{array} \right) \text{C}_6\text{H}_5 \text{Cl} \left( \begin{array}{c} \text{OR} \\ \text{OR'} \\ \text{OCH}_3 \end{array} \right) \text{C}_6\text{H}_5 \text{Cl} \left( \begin{array}{c} \text{OR} \\ \text{OR'} \\ \text{OCH}_3 \end{array} \right) \left( \begin{array}{c} \text{OCH}_3 \\ \text{(CH}_2)_n\text{SH} \end{array} \right) \right) \]

\[ R = \text{C}_{16}\text{H}_{33} \quad R' = \text{C}_8\text{H}_{17} \]

Donor - Chromophore - Acceptor Ensemble

**Scheme 1.IV.** Good candidate molecules for molecular wire studies: a rigid rod polymer molecule for examining intramolecular conductivity, and an imagined donor-chromophore-acceptor ensemble for examining intramolecular electron transfer and charge separation.
To perform the task of anchoring and orienting the bridging molecule adequately, the end groups will have to meet certain criteria. First, they will have to attach to the surfaces of their complimentary electrode materials with high selectivity, irreversibility, and electrochemical robustness. It is also important that the functional groups be synthetically accessible. An additional restriction introduced into model systems for studying OSA with monolayers is that the self-assembly occur with the attachment groups at equal concentration. It is also important that the materials required as substrates be conductors compatible with microfabrication techniques. These last two requirements were the shortcomings of the previously examined systems for orthogonal self-assembly.\textsuperscript{7,8} Scheme 1.V is a pair of computer-generated pictures showing the rigid rod molecule and donor-chromophore-acceptor molecule of Scheme 1.IV orthogonally self-assembled in the gap between a pair of microelectrodes.

This thesis details the development of two new systems for the orthogonal self-assembly of monolayers. We have demonstrated that thiols and carboxylic acids selectively self-assemble from a common solution onto microelectrode arrays of interdigitated Au and indium tin oxide electrodes (ITO) on a Si\textsubscript{3}N\textsubscript{4} substrate with the thiols attaching only to exposed gold surfaces and the acid attaching only to the ITO. Phosphoric acids bind to ITO with selectivity equal
Scheme 1.V. A pair of computer-generated pictures showing the rigid rod molecule and donor-chromophore-acceptor molecule of Scheme 1.IV orthogonally self-assembled in the gap between a pair of microelectrodes.
to that of the carboxylic acids, but with more aggressive attachment.

Chapter 2 describes the microfabrication procedure for the ITO microelectrode arrays essential to this work and gives examples of microelectrode array designs which are optimized for specific electrochemical uses.

Chapter 3 reports selective monolayer formation on ITO microelectrode arrays by electroactive carboxylic acids. Monolayer formation and selectivity were verified by cyclic voltammetry and Auger electron spectroscopy. ITO's primary advantages over the Al₂O₃ used in the previous OSA study are its ability to be used as an electrode and the large body of processing knowledge which exists for it. This report reiterates the dependence of monolayer formation on proper substrate preparation.

The orthogonal self-assembly of monolayers of thiols and either carboxylic acids or phosphonic acids on Au and ITO surfaces is described in Chapter 4. Cyclic voltammetry, Auger electron spectroscopy (AES), and secondary ion mass spectrometry (SIMS) are used to characterize the monolayers and verify their orthogonal self-assembly.

Finally, measurement of the diffusion of Ag⁺ in frozen HClO₄ · 5.5 H₂O electrolyte is reported in Chapter 5. This study used microelectrode arrays optimized for work in solid state and high-resistance media. The frozen HClO₄ · 5.5 H₂O electrolyte was found to contain at least two
phases with domains larger than the 80µm microelectrode array, and may provide insight into the phenomena of ionic diffusion in solids.
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Chapter 2

Microfabrication of Micron-Scale Gold/Indium Tin Oxide Interdigitated Microelectrode Arrays and Rational Microelectrode Design
Introduction

The extensive body of microfabrication technology which has been developed for the production of integrated circuits has been successfully adapted to the production of microelectrode structures in the field of electrochemistry. Many researchers have demonstrated a proficient application of microfabrication technology to produce microelectrode arrays for use in electrochemical experiments, beginning with Wohltjen's review of devices mostly adapted from solid state microelectronics,¹ and later by the groups of Murray,² Majda,³ Faulkner,⁴ and preeminently the work of Wrighton and co-workers in this laboratory.⁵ The resulting microfabricated electrochemical devices have been used in a wide variety of experiments, including conducting polymers and molecular electronics,⁶ sensors,⁷ and monolayer studies.⁸

This chapter first will summarize the general procedure for the fabrication of microelectrode arrays. Then, as Part 1, we wish to report a new microfabrication process for patterning indium tin oxide as an electrode material for use in micron-scale microelectrode arrays. Finally, in Part 2, we will discuss and give examples of the design and microfabrication of microelectrode arrays tailored for specific types of experiments, an approach referred to here as rational microelectrode design.
General Procedures For The Fabrication of
Microelectrode Arrays

The methodology for preparing microelectrode arrays with eight individually addressable gold or platinum electrodes (0.1 μm thick, 80 μm long, 2 μm wide, separated by 1.5-2 μm) on silicon nitride/silicon oxide/p-type silicon substrates has been reported previously. This procedure was followed to produce all of the microelectrode arrays described in this chapter except where variations in fabrication due to the use of ITO, silicon, or shadow deposition are presented.

Masks for photolithography were designed using the KIC program running on a Tektronics 4125 workstation in the department of electrical engineering at the Massachusetts Institute of Technology. Design files were transferred electronically in the .MANN format to a technician-run GYREX e-beam mask pattern generator. Reticles for stepping (10X) photolithography were generally done in emulsion, while contact masks were in chrome.

Substrates for the arrays were four inch single crystal silicon wafers processed in the Integrated Circuits Laboratory of the department of electrical engineering at the Massachusetts Institute of Technology. To insure good insulating properties on the substrates, the wafers were first modified with 5000 Å of thermally grown oxide, then coated with 1500 Å of LPCVD silicon nitride.
First layer photolithography was performed on the four inch wafers using a GCA MANN Model 4800 DSW Wafer Stepper and a GCA Model 1006 Wafertrac in the MIT Integrated Circuits Laboratory. A focus setting of 213 (arbitrary units) and exposure time of about 0.200 s were typical.

Contact photolithography for second layer depositions was done using a Headway Research spin station and KTI or Shipley photoresist. Exposures were done on a Karl Suss contact mask aligner.

Metallization in all cases was done using a Sloan multiple-hearth electron beam evaporator with a quartz crystal thickness monitor, operating at about $10^{-7}$ to $10^{-6}$ torr. A light 60 watt, 20 s "de-scum" oxygen plasma cleaning of the photoresist prior to metal deposition was critical for successful lift-off. Lift-off proceeded in acetone for 2 to 120 minutes depending on the materials deposited, often with the aid of sonication.

Wafers of finished devices were diced carefully by hand using a diamond scriber and snapping the substrates. Semi-automated diesaw cutting proved problematic. Mounting of the arrays for use in electrochemical experiments was done by hand using conductive silver epoxy (Epoxy Technology) to make electrical contact and chemically resistant epoxy (Hysol) for final encapsulation on 8-pin headers attached to appropriately sized glass tubing.
Part 1: The Fabrication of ITO Microelectrode Arrays

Introduction

Indium tin oxide is a material frequently used in microfabrication as well as electrochemistry because of its unique properties. It is a clear, conductive, relatively unreactive metal oxide comprised of a mixture of typically ninety-one percent indium oxide (In₂O₃), in combination with a balance of tin oxide (SnO₂). It is similar to other semiconducting metal oxides such as indium oxide or tin oxide used alone, but exhibits slightly superior properties.¹⁰

It is most often used as a thin film material in many types of electronic devices, including electrochromic displays,¹¹ solar cells,¹² microelectronics,¹³ heat mirrors,¹⁴ and gas sensors.¹⁵ The broad utility of ITO has spurred the growth of a body of general processing knowledge,¹⁰ while increasingly competitive international interest in the commercial application of ITO technology in flat panel display (FPD) devices for use in computers and video systems has resulted in much of the specific new device technology in the area being patented.

Less secretly, ITO also is used as an electrode material in electrochemical cells in conjunction with spectroscopic studies requiring an optically transparent electrode (OTE),¹⁶ or when an experiment calls for
electrode potentials which would cause faradaic interference such as oxidative or reductive gas evolution from standard platinum or gold electrodes.

While ITO's utility as a conventional electrode material is evident, a relatively unexploited property of the material is its surface chemistry. Several researchers have begun to study the surface chemistry of ITO or the related metal oxides,\textsuperscript{17} but the volume of work is considerably smaller than that directed to the gold/thiol system, for example. ITO, being a metal oxide, could be expected to behave differently at its surface than common zero-valent metal electrodes like gold or platinum.\textsuperscript{17c} It is this difference that can be exploited in order to devise a system for orthogonal self-assembly (OSA) of monolayers at electrode surfaces.

Orthogonal self-assembly is the simultaneous but independent formation of two self-assembled monolayers (SAMs) adsorbed from a common solution onto a substrate exposing two different materials at its surface. Orthogonal self-assembly of monolayers has been previously demonstrated in our laboratory on gold and non-conductive alumina surfaces using substituted thiols and carboxylic acids, respectively,\textsuperscript{8b} and also with gold and platinum oxide structures using terminal disulfide and isocyanide functional groups in non-stoichiometric ratio as the means of establishing surface attachment.\textsuperscript{8d}
A logical progression in the technology would be to find such a system for OSA that could ultimately be used for the self-assembly of "molecular wires" oriented between two electrodes. The minimum requirements for such a system would be the following: the respective adsorptions will be highly selective from equimolar solutions; the anchoring head groups will form strong, effectively irreversible, electrochemically robust connections with the surface of an electrode; the functional groups making the connections will be synthetically accessible; and handling factors such as solubilities will be reasonable and workable.

Based on the body of previous work, ITO was judged a good candidate to become part of a system for orthogonal self-assembly of monolayers, and ultimately part of the technology necessary for the realization of molecular wires.

**Microfabrication Process for ITO Microelectrode Arrays**

The common methods in use for depositing ITO thin films are sputtering\(^1\) (RF, dc magnetron) or evaporation\(^2\) (electron beam, thermal). A consideration in the processing of ITO thin films is the loss of oxygen during the deposition and formation of reduced sub-oxides in the film.\(^3\) The sub-oxides degrade the ITO's conductivity and optical transparency. Film quality can be maintained by conducting the evaporation under a partial pressure of
oxygen (10^-3 to 10^-4 torr) while heating the substrate to a temperature of 200 to 400 °C (reactive evaporation), or less successfully, by annealing the film in the presence of oxygen after the deposition.

Patterning of ITO is almost always done by either a masked wet etching process using halo-acids21 with resolution down to tens of microns, or a dry etch process22 (plasma, sputtering, or reactive ion) often with similar reagents and resolution in the micron range. Lift-off patterning,23 while frequently used for thin metal films, is rarely used with ITO because of the incompatibility of the film deposition conditions (e.g. substrate heated to 200-300 °C) with conventional photoresists, which degrade at elevated temperatures.

We have been able to lift-off pattern ITO thin films using conventional photoresist to make microelectrode arrays by using a sequential multi-layer electron beam deposition technique which results in an ITO-gold-ITO sandwich structure of high conductivity. This process is outlined in Scheme 2.I. ITO deposition was carried out in the MIT Center for Materials Science and Engineering Microelectronic Technology Central Facility on a Sloan multiple source electron beam evaporator operating at 10^-6 torr with a quartz crystal thickness monitor. ITO (ninety-one mole percent In2O3, nine mole percent SnO2) was obtained in chunk form from Cerac, Milwaukee, Wisconsin. The ITO was sublimed from a quartz crucible using a
Scheme 2.1. Top: the fabrication sequence for ITO microelectrode arrays patterned by a lift-off process. Bottom: cross-sectional representation of an ITO microelectrode showing the ITO/gold/ITO layer structure.
broadly-focused electron beam to avoid scattering the pieces. Fifty angstroms of Cr or Ti metal was deposited as an adhesion layer before each ITO or gold run. Lift-off proceeded by soaking the wafer in acetone and sonicating, finishing the fabrication of the arrays, Figure 2.1.

Sheet resistivities for films of a total thickness of about 1500 Å with 500 Å of gold between the ITO layers were 150Ω/square without reoxidation and 75Ω/square with reoxidation at 300°C for two to four hours in air, which is comparable to resistivities reported for high quality ITO films deposited by conventional methods. Films deposited without the gold conduction layer had sheet resistivities of 900Ω/square as deposited and 500Ω/square with reoxidation. Although the resistivities of the films varied as much as fifty percent from run to run, the sample incorporating the gold layer always displayed significantly greater conductivity than the pure ITO film.

The photolithography process makes a resist profile which is slightly trapezoidal, making it an artifact of the lift-off process that the first layer deposited will comprise the outside vertical surface of the patterned features. The three layer ITO-gold-ITO sequence, rather than a simpler gold-ITO two layer process, is required to insure that ITO and not gold is present on all geometric surfaces of the electrodes, as shown in Scheme 2.I. The thin strip of residual gold at the lift-off fracture line has proven undetectable by SEM, Auger, or electrochemical
Figure 2.1. Scanning electron microscope (SEM) photomicrographs of the active electrode area of an ITO microelectrode array.
techniques and has therefore been judged inconsequential to the function of the arrays.

The technique of using a metal layer beneath an ITO layer to enhance conductivity has since been applied to connecting features in active matrix flat panel displays.\textsuperscript{24}

**Electrochemical Characterization**

The electrochemical response of the microfabricated ITO structures and thin films was examined by cyclic voltammetry under varied conditions. Figure 2.2 shows cyclic voltammograms of a plain ITO macroelectrode and an ITO/Au/ITO electrode exposed to a solution of one millimolar ferrocene in acetonitrile. The relative magnitudes of the baseline charging currents and peak separation for the oxidative and reductive halves of the waves are indicative of the lower resistivity and more ideal behavior of the ITO/Au/ITO electrode.

Figure 2.3 shows baseline scans of a commercial transparent tin oxide macroelectrode (5mm x 20mm, Delta Technologies, Stillwater, Minnesota) and an ITO/Au/ITO microelectrode. The useful potential window in aqueous buffered (pH7-phosphate) potassium chloride electrolyte for the microelectrode is comparable to the commercial material at the positive extreme and extended about four hundred millivolts at the negative cut-off. This baseline electrochemical response is very similar to that reported in the literature.\textsuperscript{16} The electrochemical response of the
Figure 2.2. Cyclic voltammograms of ITO macroelectrodes (200 mV/s) in CH₃CN/0.1 M (n-Bu₄N)PF₆ with 10⁻³ M ferrocene. The voltammogram on the left is from an electrode prepared by the e-beam evaporation of a single layer of ITO onto a silicon nitride substrate, and the voltammogram on the right is from an electrode with ITO/gold/ITO deposition layers.
ITO Macroelectrode Solution Electrochemistry

1mM Ferrocene vs. silver wire reference
Acetonitrile/0.1M (n-Bu)4 NPF6 electrolyte
Scan Rate 200mV/sec
Figure 2.3. Cyclic voltammetry baseline scans (10 mV/s) for an electrode made from commercial tin oxide on glass (top) and an e-beam deposited ITO/gold/ITO microelectrode in aqueous, buffered (pH7 - phosphate) 0.1 M KCl electrolyte.
Baseline scans at 10 mV/sec
Aqueous 0.1 M KCl, pH 7 (phosphate buffer)

Commercial SnO₂ on Glass

Indium-tin Oxide Microelectrode

Current, µA

Current, nA

Potential, V vs. SCE
individual electrodes in the microelectrode array toward a solution of five millimolar Ru(NH3)6Cl3 was nearly ideally sigmoidal, Figure 2.4, and diffusion limited as previously reported for similar structures made of gold or platinum.25

Part 2: Rational Microelectrode Design

Introduction

Microfabricated microelectrode arrays used in electrochemical experiments in the last decade have taken many forms. Earlier experimental attempts with fabricated microelectrodes were hybrid devices adapted from solid state electronics for sensor research, as detailed in the review article by Wohltjen.1 Most reported examples consist of two interdigitated multifingered electrodes with features in the size scale of several microns.2,3 The most versatile example of microelectrode arrays to date has been the design featuring eight individually addressable microband electrodes (0.1 μm thick by 80 μm long by 2 μm wide separated by 2 μm) produced in this laboratory by Kittlesen5a and later modified by Schloeh. The types of experiments performed with these arrays have been wide-ranging.6,7,8

Here I wish to report on some new variations of the Schloeh array design and three entirely new array designs produced for use in specific types of experiments not well served by the standard eight electrode array.
Figure 2.4. Individual cyclic voltammograms (50 mV/s) for all eight electrodes of an e-beam deposited ITO/gold/ITO microelectrode array in a 5 mM solution of Ru(NH$_3$)$_6$Cl$_3$ in aqueous buffered (pH7 - phosphate) 0.1 M KCl electrolyte.
ITO/Au/ITO Microelectrode Solution Electrochemistry

5mM Ru(NH$_3$)$_6$Cl$_3$ vs. SCE
Aqueous 0.1M KCl/pH (phosphate)
Scan Rate 50mV/sec
Microelectrode Arrays With Silicon "Capped" (Top Insulated) Electrodes

Figure 2.5 shows SEM photomicrographs of a standard eight-electrode platinum microelectrode array (electrodes 0.1 μm thick by 80 μm long by 2 μm wide separated by 2 μm) with the additional deposition of a 500 Å layer of silicon evaporated over the metal before lift-off. The silicon, because it quickly forms a native oxide, passivates the tops of the electrodes to electrochemical reactions while the edges of the electrodes remain active. In Figure 2.5, electrochemical plating of palladium metal is visible around the perimeter of selected electrodes, but no metal has been plated on the tops where the silicon had been deposited. Figure 2.6 shows an SEM photomicrograph and two Auger element maps of the same structure showing the localization of the palladium at the edges of the plated electrodes.

Chunk silicon (Aldrich, Milwaukee, WI) was melted in a graphite crucible in a Sloan e-beam evaporator operating at 10⁻⁶ torr and electron-beam evaporated to a thickness of 500 Å after a 50 Å chromium or titanium adhesion layer. The silicon was the last layer deposited on a platinum microelectrode array prepared by previously reported procedures.⁵,⁹ Lift-off proceeded as usual, and an oxidizing step of either annealing in an oven at 200 to 300 °C in air or placing the sample in an oxygen plasma could be done to augment the thickness of the oxide on the
Figure 2.5. SEM photomicrographs of a platinum microelectrode array electroplated with palladium metal on the edges of five of the electrodes. The tops of the electrodes were passivated by an e-beam deposited layer of silicon.
Figure 2.6. SEM photomicrographs and scanning Auger element maps of silicon and palladium for a platinum microelectrode array electroplated with palladium metal on the edges of alternate electrodes. The tops of the electrodes were passivated by an e-beam deposited layer of silicon.
silicon, but neither enhanced the passivation provided by the silicon overlayer exposed only to ambient conditions.

**Ultrasmall Gap Silicon "Capped" (Top Insulated) Microelectrode Arrays Produced By the Shadowing Technique**

The shadow deposition technique for depositing metal on the electrodes of an existing microelectrode array for the purpose of greatly reducing the inter-electrode spacing has been demonstrated in this group and thoroughly reported. This procedure is outlined in Figure 2.7 and a finished device is shown in Figure 2.8. In the previous work, a second shadowed layer of insulating SiO₂ or Al₂O₃ deposited at a different angle on the electrodes was used to passivate the tops of them while leaving only a small active area of exposed metal at the edges. The reduced electrode area and shortened inter-electrode spacing enhanced the switching speed of conducting polymers deposited in the gap between adjacent electrodes by virtue of the smaller amount of material necessary to make the connection.

A problem with using silicon oxide or alumina as the insulating layer is the tendency of non-monatomic species to undergo decomposition in the electron beam evaporation process, e.g. to form suboxides in the case of metal oxides. This is analogous to behavior reported for e-beam evaporated ITO. These decomposition species tend to
Figure 2.7. A cross-sectional drawing of a gold microelectrode array modified first with shadow-deposited gold and then shadow-deposited silicon for the purpose of reducing the inter-electrode spacing and passivating the tops of the electrodes.
(a) AS FABRICATED

(b) Au SHADOWED

(c) Si SHADOWED
Figure 2.8. SEM photomicrographs of a platinum microelectrode array modified first with shadow-deposited platinum and then with shadow-deposited silicon.
scatter more and deposit in a manner which is less "line-of-sight" than monatomic species like Au, Pt, or Si.

Extensive effort trying to image the small exposed active metal area on the electrodes of shadowed insulated small gap microelectrode arrays made with SiO₂ or Al₂O₃ proved futile. It is hypothesized that the SiO₂ or Al₂O₃, in the process of being degraded in the electron beam, forms particles or species which scatter enough to coat the metal electrode area under the shadow edge with sufficient thickness to preclude effective analysis by Auger, but not greatly enough to prohibit electrochemical reactions from taking place through the pores in the film.

Silicon, being a monatomic species, does not undergo any e-beam induced degradation and shadow deposits in a more truly line-of-sight fashion. Figure 2.9 shows an SEM photomicrograph and two Auger element maps for silicon and platinum taken from a shadowed silicon-on-platinum-on-platinum device. The platinum map clearly indicates the small exposed active area of the electrodes.

An Eight Electrode Microelectrode Array With Auxiliary Electrodes ("tg10")

Figure 2.10 shows a photomicrograph of a microelectrode array composed of eight electrodes: six of which are working electrodes 0.1 μm thick by 80 μm long by 2 μm wide, separated from each other by 2 μm; one utility electrode surrounding the array of working electrodes at a
Figure 2.9. SEM photomicrographs and scanning Auger element maps of silicon and platinum on a platinum microelectrode array modified with shadow-deposited platinum and silicon.
Figure 2.10. Photomicrographs of an eight electrode microelectrode array with two of the electrodes designed as utility electrodes. The parallel electrodes in the bottom picture are 80 μm long, 0.1 μm thick, 2 μm wide, and separated by 2 μm.
distance of 8 μm; and one large 3 x10^5 μm^2 electrode 400 μm distant from the array of working electrodes. The largest electrode, having nearly 2000 times the area of each of the working electrodes and being removed by some distance, can easily be used as a counterelectrode, while the utility electrode close to the array can be plated with silver for use as a quasi-reference electrode.

Having all these electrodes of favorable geometry present on the same chip makes this device design ideally suited for experiments in which having working, counter, and reference electrodes present in a small area is desirable, such as in a cell using solid electrolyte. This device has been successfully used in experiments making fully contained sensors in solid electrolyte^7a and in transit time measurements in solid electrolyte, described in chapter 5 of this thesis.

**A Large Active Area Interdigitated Microelectrode Array ("tg17")**

Conductivity measurements of polymer films with only moderate conductivity require more active electrode area than a small array of microelectrodes can provide. Figure 2.11 shows two photomicrographs of an eight electrode interdigitated microelectrode array which in its fully interdigitated configuration presents an active electrode area 1.5mm by 2.3mm, approximating two linear electrodes over 21cm long, separated by 4 microns. Arrays of closely
**Figure 2.11.** Photomicrographs of an eight electrode interdigitated microelectrode array. The separation between the individual interdigitated electrodes is 4 μm.
spaced microelectrodes have proven useful for in situ measurements of conductivity of polymer films. The array design depicted here has been successfully used to measure conductivities of solution-cast films of varying length polyacetylenes.

An Edge-Connectable Microelectrode Array ("tgif")

The microelectrode array pictured in Figures 2.12 and Figure 2.13 is an attempt to simplify the usual procedure of making electrical contact and encapsulating microelectrode arrays with carefully hand-applied epoxy. The device shown uses electrode leads which at their ends match the pitch of a push-connect socket similar to the type used on printed circuit boards, thus avoiding connections to the chip made with silver epoxy.

This design has seven working electrodes 4 μm wide and 100 μm long, separated from one another by 2 μm, in an array located at the bottom of a 1cm by 1 cm chip, opposite the connection points on the leads. The design also has one large area electrode of about 10 mm² for use as a counter electrode. It also incorporates an area of microfabricated test structures including grids, bands, and checker boards of varying dimensions for use in surface chemistry experiments where resolution is of importance. This microelectrode array design has been used successfully for high resolution secondary ion mass spectrometry imaging of surface-adsorbed monolayers.
Figure 2.12. Photomicrograph of a 1cm x 1cm eight-electrode edge-connect microelectrode array.
Figure 2.13. Photomicrographs of the microelectrodes of an eight-electrode edge-connect microelectrode array.
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Chapter 3

Spontaneous Monolayer Formation on Indium Tin Oxide Microelectrode Arrays by Substituted Carboxylic Acids with Characterization by Electrochemistry and Auger Surface Spectroscopy
**Introduction**

We wish to report the selective formation of self-assembled monolayers (SAMs) on indium tin oxide (ITO) microelectrode arrays by molecules I and II terminated with

![Chemical structures](image)

a carboxylic acid, -COOH, functional group. The self-assembled monolayers described here are a means of surface modification whereby a single layer of molecules spontaneously chemisorbs in a more or less ordered way onto a surface from a solution containing the adsorbate molecule, Scheme 3.I. This data joins the body of previously reported studies from this and other laboratories of SAM formation on materials by functionalized molecules, e.g., silanes on metals, semiconductors, and insulators;\(^1\) isonitriles on Pt;\(^2\) dithiocarbamates on Pt;\(^3\) thiols and disulfides on Au;\(^4\) and carboxylates on metal oxides.\(^5\) The work of many researchers has shown that SAMs are a versatile method of surface modification.\(^6\)
Scheme 3.I. The spontaneous, selective formation of a monolayer of molecule L on an ITO microelectrode on a Si$_3$N$_4$ substrate, shown in cross section.
This report detailing the procedure for forming and characterizing carboxylate monolayers on ITO will extend work performed in this laboratory to develop systems for orthogonal self-assembly (OSA).\textsuperscript{5c,7} The previously reported system, in making use of thiol-terminated molecules adsorbing to Au and carboxylic acid molecules adsorbing to native Al\textsubscript{2}O\textsubscript{3} present on Al metal,\textsuperscript{5c} had the important limitation of Al not being able to serve as an electrode for electrochemistry. Ultimately, by using ITO, a viable material for use in electrochemistry and electronic microfabrication, instead of Al\textsubscript{2}O\textsubscript{3} on Al in such a system for orthogonal self-assembly, it is hoped that the technology which may someday lead to molecular wires, single molecules oriented in the gap between very small pairs of microelectrode array,\textsuperscript{8} will inch forward.

**Experimental**

**ITO Macroelectrodes and Microelectrode Arrays**

Both the detailed description of the fabrication of the ITO microelectrode arrays used in this study and the use of carboxylate monolayers on ITO in a system for orthogonal self-assembly are reported elsewhere in this thesis. In brief, the indium tin oxide (ITO) microelectrode arrays, consisting of eight individually addressable band microelectrodes, ~2μm wide, 0.15μm high, 80μm long, and separated from one another by ~2μm, are
prepared using microfabrication techniques similar to those previously reported. After lithographic patterning, it is necessary to deposit the ITO (91% In2O3 and 9% SnO2 in chunk form from Cerac, Milwaukee, WI) in a multilayer e-beam lift-off procedure incorporating a layer of Au between two ITO layers, in order to make electrodes which have good conductivity while only exposing ITO at their outside surfaces. Patterning the arrays in an e-beam lift-off process with only a single layer of ITO was not deemed practical because of the incompatibility of the conventional photoresist used here with the elevated substrate temperatures (200-300 °C) generally required in order to deposit highly conductive, good quality ITO films by electron beam evaporation. Hence, making the ITO microelectrode arrays with an ITO/Au/ITO multilayer deposition allowed us to use our conventional e-beam lift-off process to pattern the features.

Deposition of Monolayers

Molecule I was obtained from Dr. Eric Wollman of M.I.T., who synthesized it using conventional methods, and II is available commercially (Aldrich, Milwaukee, WI). Monolayers of I or II can be self-assembled onto ITO micro- or macroelectrodes from 10^{-3} M solutions in iso-octane or 1:1 ethanol:hexane in ~18 hours. All solvents were freshly distilled and were generally kept under a flow of Ar or N2
gas, but techniques to maintain rigorous dryness were not used.

The preparation of the electrode surface prior to the adsorption had a significant effect on the coverage and electrochemistry of the resulting monolayers. Cyclic voltammograms of I adsorbed onto ITO macroelectrodes pre-treated in a Harrick plasma cleaner/sterilizer operating at the medium (60 W) setting with O₂, Ar, and H₂ plasmas alone or in combination vary significantly, Figure 3.1. The cleaning procedure used was an ultrasonic cleaning in acetone for 5 to 30 minutes, followed by 3 to 10 minutes exposure to a 60 W Ar plasma and finishing with 1 to 5 minutes at 60 W in an H₂ plasma. The electrodes would then be introduced immediately to the deposition solution.

The ITO microelectrodes were particularly sensitive to adventitious forms of dirt. Great care had to be taken during the microelectrode array mounting procedure to minimize exposure to outgassing from epoxies, and cleaning times for the microelectrode arrays generally needed to be longer than those required for the macroelectrodes.

**Characterization by Cyclic Voltammetry**

All electrochemistry was done in closed round bottom flasks purged with argon using a PINE RDE4 bipotentiostat connected to a Pt gauze counter electrode and Ag wire reference electrode. The electrolyte was recrystallized
Figure 3.1  Cyclic voltammograms of 5 ITO macroelectrodes of nearly equal area derivatized with I after exposure to various plasmas, as labeled. The changes in plasma pretreatments caused significant variations in monolayer coverage and peak splitting in the cyclic voltammograms.
Effect of Plasma Cleaning on Monolayer Formation on ITO

\[ \text{Acetonitrile/OIM (n-Bu)4PF}_6 \]
vs. Ag wire
500 mV/sec
1 mM \( \text{Fc(CH}_2\text{)}_{11}\text{COOH} \) in
1:1 ethanol:hexane
18 hours
tetrabutylammonium hexafluorophosphate, 0.1 M in freshly distilled acetonitrile. Prior to cyclic voltammetry, all ITO electrodes were rinsed thoroughly with hexane upon removal from the monolayer deposition solution.

**Characterization of Carboxylate Monolayers on ITO by Scanning Auger Spectroscopy**

Auger analysis was done using a Perkin Elmer Phi 660 Scanning Auger Microprobe operating at beam voltages of 5-10 kV and beam currents of 3-5 nA to minimize damage to the monolayer.\(^5c\) Samples were affixed to small pieces of copper foil with Ag paint to minimize charging.

**Results and Discussion**

It is interesting to note from Figure 3.1 that an O\(_2\) plasma is not the best cleaning treatment for the ITO, as judged from surface coverage, peak splitting, peak symmetry, and background current observable in the cyclic voltammograms. This is surprising because intuitively, an oxidizing O\(_2\) plasma and the ITO metal oxide seem compatible. The H\(_2\) plasma, and to a lesser extent the Ar plasma precleanings, however, result in better electrochemical response from the resulting monolayers. This may be because the H\(_2\) plasma is better able to populate the oxide surface with active, dangling, \(-\text{OH}\) groups which promote monolayer formation through an ester-
type linkage with the carboxylic acid functionality on the adsorbate molecules,\textsuperscript{5d} while the oxygen plasma removes active \(-\text{OH}\) groups and forms more of a "hard" oxide which is not quite as reactive. The \text{Ar} plasma is perhaps in between the two, neither enhancing nor retarding surface reactivity.

Figure 3.2 shows cyclic voltammograms for an ITO electrode exposed to ferrocene in solution and another ITO electrode derivatized with a monolayer of I by the above procedure and cycled in blank electrolyte. The surface confinement of the ferrocene in the monolayer is confirmed by the narrow peak splitting and the return to background current after the reductive or oxidative halves of the wave. Surface coverage was calculated to be \(\sim 4 \times 10^{-3}\) mol cm\(^{-2}\), or about one monolayer of material. Scanning for long periods results in loss of surface coverage; up to half of the signal could be lost after scanning for \(\sim 30\) minutes. Other work has shown, however, that ferrocene-terminated carboxylic acids with longer hydrocarbon chains than I show improved durability.\textsuperscript{12}

Figure 3.3 shows the set of cyclic voltammograms obtained from the eight electrodes of an ITO microelectrode array derivatized with I. Surface coverages for the individual electrodes averaged \(6 \times 10^{-10}\) mol cm\(^{-2}\), while the integrated current from all eight scanned together equaled the sum of that from the individual electrodes.
Figure 3.2. Comparison of the electrochemical responses of similar ITO macroelectrodes toward a surface confined monolayer of I (an alkylferrocene, left), and ferrocene in solution (right).
ITO Macroelectrode

Derivatized for 18 hours in 1 mM Fe(C₆H₄)₃ COOH/1 l ethanol/hexane vs. Ag wire reference Acetonitrile / 0.1M (n-Bu)₄ NPF₆ 500 mV/sec

1 mM Ferrocene solution vs. Ag wire reference Acetonitrile / 0.1M (n-Bu)₄ NPF₆ 200 mV/sec

Current, µA

Potential, V vs. Ag wire
Figure 3.3. Electrochemical responses of all eight electrodes on an ITO microelectrode array derivatized with a self assembled monolayer of I. Average surface coverage of the microelectrodes is $\sim 6 \times 10^{-10}$ mol cm$^{-2}$. 
ITO/Fc(CH₂)_11 COOH
CH₃CN/O.1 M [(n - Bu)_4 N]PF₆

Derivatized from 1 mM solution in 1:1 hexane:ethanol
20 hours

500 mV/sec

Current, nA

All Electrodes

Potential, V vs Ag wire

Current, nA

Potential, V vs Ag wire
Auger electron spectroscopy (AES) uses a highly focussed electron beam to examine the elemental composition of surfaces. AES was used in this series of experiments to detect the presence of II self-assembled onto the ITO microelectrodes of an eight electrode microelectrode array, and to determine the degree of selectivity for adsorption of II between ITO and the exposed Si₃N₄ surface by confirming II's absence on the Si₃N₄ substrate. Molecule II was chosen for the Auger studies because the perfluorination makes it easily detectable by AES compared to I, which has no good Auger "tag" element. C, O, and N are too prevalent in nature to be useful for surface analysis in most cases.

Figure 3.4 shows survey spectra taken on the ITO and Si₃N₄ surfaces of an ITO microelectrode array derivatized in a 10⁻³ M solution of II in hexane for 18 h. Comparison of the two spectra shows F present on the ITO surface but not the Si₃N₄, confirming the selective adsorption of the carboxylic acid monolayer. Element mapping by Auger rapidly rasters the analyzing beam across the sample and assigns to each pixel a brightness value proportional to the intensity of the detected signal for a specified element. Auger element mapping for the elements F and In shows the registration of the F signal with the ITO electrode structures, and its absence on the underlying Si₃N₄ substrate, Figure 3.5.
Figure 3.4. Auger electron spectroscopy (AES) survey spectra taken from an ITO microelectrode array fabricated on a Si$_3$N$_4$ substrate and derivatized with II. The presence of the F signal in the ITO surface survey spectrum and its absence in that from the Si$_3$N$_4$ surface confirm the selectivity of the adsorption of II.
ITO Device Derivatized with $\text{CF}_3(\text{CF}_2)_8\text{COOH}$

Si$_3$N$_4$ Region

Counts, arbitrary units

Kinetic Energy, eV

ITO Region

Counts, arbitrary units

Kinetic Energy, eV
Figure 3.5. Auger electron spectroscopy element maps for F and In taken from an ITO microelectrode array fabricated on a Si3N4 substrate and derivatized with II. The F signal from the monolayer of II is in registration with the In signal from the microelectrodes, confirming its confinement to the ITO electrode structure and its absence on the underlying Si3N4 substrate.
Conclusions

We have shown that substituted carboxylic acid molecules will spontaneously form electroactive self-assembled monolayers on ITO microelectrodes fabricated on an insulating Si$_3$N$_4$ substrate with great selectivity. The ITO/carboxylic acid system for the self-assembly of monolayers on metal oxides will prove complimentary to existing techniques for derivatizing metal surfaces, and will be another tool for tailoring surfaces in combination with microfabrication techniques.
References


5. (a) Allara, D.; Nuzzo, R. Langmuir 1985, 1, 45. (b) Allara, D.; Nuzzo, R. Langmuir 1985, 1, 52. (c) Laibinis, P.; Hickman, J.; Wrighton, M.; Whitesides,


Chapter 4

Systems for Orthogonal Self-Assembly of Electroactive Monolayers
Introduction

In this chapter, we wish to report on systems for the independent formation of two self-assembled monolayers on two different materials exposed to adsorbate molecules present in a single solution. This work, using electroactive adsorbate molecules and functional electrode materials, extends previous efforts in this laboratory in the area of orthogonal self-assembly (OSA) of monolayers.¹

A self-assembled monolayer (SAM) is a single layer of molecules spontaneously chemisorbed to the surface of a substrate exposed to a solution of the adsorbate molecule, L, as shown in Scheme 4.I. Many examples of functionalized molecules and substrate materials which react this way to form SAMs have been reported.² Our interest in SAMs lies in exploiting differences in the reactivity of functional groups on molecules together with the reactivity of exposed substrate surfaces to achieve selective monolayer formation. Scheme 4.Ia illustrates the adsorbate L reacting with an electrode, but not the underlying substrate, to form a monolayer.

To imagine a molecular-scale device with some sort of electronic³ or sensing function, an even greater degree of control over the molecules of interest could be necessary. Orthogonal self-assembly is independent SAM formation on different areas of a substrate with two or more molecules
Scheme 4.1. (a) A cross-sectional representation of monolayer formation by molecule L on a microelectrode on a substrate. (b) Orthogonal self-assembly of molecules $L_1$ and $L_2$ onto electrodes made of two different materials.
from a single solution, Scheme 4.Ib. In this example, \( L_1 \) binds selectively and exclusively to one of the exposed materials while \( L_2 \) behaves similarly toward another, and neither bind to the substrate. The first such system reported used thiol molecules (\( L_1 \)) to bind to Au structures and carboxylic acid molecules (\( L_2 \)) to bind to insulating Al\(_2\)O\(_3\) on Al structures.\(^{1a}\) This chapter details research into systems for orthogonal self-assembly using molecules I-V in combination with structures made of Au and indium tin oxide (ITO), a conducting metal oxide suitable for electrochemical work.\(^4\)
Tailoring surfaces for function by this method could be done right to the size limits imposed by existing microfabrication technology. As it becomes possible to manufacture structures approaching the molecular size scale, OSA as a means of surface modification may prove useful to orient molecules between dissimilar metals to achieve electronic or non-linear optical effects, or to study electron transfer and conduction in molecules of interest.

**Experimental**

**ITO and Au Macroelectrodes and Interdigitated ITO/Au Microelectrode Arrays**

Preliminary experiments were done on ~2 cm² macroelectrodes for ease of handling. Au electrodes were made by electron beam evaporating or sputtering Au on Si₃N₄/SiO₂ coated single crystal Si wafers. The ITO was evaporated onto Si₃N₄/SiO₂ coated Si wafers as an ITO/Au/ITO multilayer using an electron beam evaporator. Alternatively, ITO on precut glass slides was obtained from Delta Technologies (Stillwater, MN).

The detailed description of the fabrication of the ITO microelectrode arrays used in this study is reported elsewhere in this thesis. In brief, the indium tin oxide (ITO) microelectrode arrays, consisting of eight
individually addressable band microelectrodes, ~2 μm wide, 0.15 μm high, 80 μm long, and separated from one another by ~2 μm, were prepared using microfabrication techniques similar to those previously reported.\(^5\) The bimetallic (Au/ITO) microelectrode arrays were prepared in a two layer process: the gold half of the array was first patterned by stepping photolithography and deposited by electron beam evaporation followed by lift-off, then the ITO was patterned by contact lithography. After lithographic patterning, it is necessary to deposit the ITO (91% In\(_2\)O\(_3\) and 9% SnO\(_2\) in chunk form from Cerac, Milwaukee, Wisconsin) in a multilayer e-beam lift-off procedure incorporating a layer of Au between two ITO layers, in order to make electrodes which have good conductivity while only exposing ITO at their outside surfaces. Patterning the arrays in an e-beam lift-off process with only a single layer of ITO was not deemed practical because of the incompatibility of the conventional photoresist used here with the elevated substrate temperatures (200-300 °C) generally required in order to deposit highly conductive, good quality ITO films by electron beam evaporation.\(^6\) Hence making the ITO microelectrode arrays with an ITO/Au/ITO multilayer deposition allowed us to use our conventional e-beam lift-off process to pattern the features.
Reagents

The method of obtaining $\text{I}$ was described in the previous chapter. Molecule $\text{II}$ is available commercially (Aldrich, Milwaukee, WI). The synthesis of $\text{II}^-$ has been reported.$^{2h}$ Molecule $\text{IV}$ was made by methods analogous to those reported by Mallouk.$^7$ Hans Biebuyck of Harvard University provided a sample of $\text{V}$. Solvents were spectroscopic grade. Electrolytes were reagent grade or better, and were recrystallized.

Deposition of Monolayers

Orthogonal self-assembly of carboxylic acids and thiols was done at concentrations of $10^{-4}$ M in each molecule (or as noted) with 1:1 ethanol/hexane, 20 percent ethanol in isooctane (by volume), or 5 percent ethanol in isooctane as solvent. All solvents were freshly distilled and were generally kept under a flow of Ar or N$_2$ gas, but techniques to maintain rigorous dryness were not used.

OSA of phosphonic acids and thiols was done at concentrations of $0.5 - 1 \times 10^{-4}$ M in each molecule from 30 percent ethanol in chloroform or from ethanol acidified with a few drops of concentrated HCl to promote solubility.

The preparation of the electrode surface prior to the adsorption had a significant effect on the coverage and electrochemistry of the resulting monolayers. Cyclic voltammograms of $\text{I}$ adsorbed onto ITO macroelectrodes pre-treated in a Harrick plasma cleaner/sterilizer operating at
the medium (60 W) setting with O₂, Ar, and H₂ plasmas alone or in combination vary significantly, as described in chapter 3 of this thesis and reported previously. ᵃᵇ A surprising finding was that prolonged or intense exposure of ITO or Au surfaces to O₂ plasma totally precluded monolayer adsorption. The cleaning procedure used was an ultrasonic cleaning in acetone for 5 to 30 minutes, followed by 3 to 10 minutes exposure to a 60 W Ar plasma and finishing with 1 to 5 minutes at 60 W in an H₂ plasma. The electrodes would then be introduced immediately to the deposition solution.

The ITO microelectrodes were particularly sensitive to adventitious forms of dirt. Great care had to be taken during the microelectrode array mounting procedure to minimize exposure to outgassing from epoxies, and cleaning times for the microelectrode arrays generally needed to be longer than those required for the macroelectrodes.

**Characterization by Cyclic Voltammetry**

For all experiments with carboxylic acids, electrochemistry was done in closed round bottom flasks purged with argon using a PINE RDE4 bipotentiostat connected to a Pt gauze counter electrode and Ag wire reference electrode. The electrolyte was recrystallized tetrabutylammonium hexafluorophosphate, 0.1 M in freshly distilled acetonitrile. Prior to cyclic voltammetry, all
electrodes were rinsed thoroughly with hexane immediately upon removal from the monolayer deposition solution.

Experiments with phosphonic acids were conducted as above, but in open top electrochemical cells. The electrolyte was 0.1 M recrystallized sodium perchlorate in 1:1 water/acetonitrile. Electrodes were rinsed with ethanol and dried after removal from the deposition solution.

Characterization of Monolayers by Scanning Auger Electron Spectroscopy (AES)

Auger analysis was done using a Perkin Elmer Phi 660 Scanning Auger Microprobe operating at beam voltages of 5-10 kV and beam currents of 3-5 nA to minimize damage to the monolayer.\textsuperscript{1a} Samples were affixed to small pieces of copper foil with Ag paint to minimize charging.

Characterization of Monolayers by Secondary Ion Mass Spectrometry (SIMS)

Secondary ion mass spectra of SAMs of IV and V on Au and ITO microstructures were obtained using a Vacuum Generators IX70S. Details of this procedure have been previously reported.\textsuperscript{2k}
Results and Discussion

Orthogonal Self-Assembly of Carboxylic Acids on ITO and Thiols on Au

The evidence presented here for orthogonal self-assembly takes two forms: electrochemical cyclic voltammograms and high vacuum surface spectroscopy. The combination of these techniques can provide information on the distribution and surface concentration of the molecules adsorbed to the structures of interest. The molecules used in this study, however, had to include unique "tags" to make them detectable by the analytical techniques being used.

Cyclic voltammetry can be used to confirm that a molecule is on a surface by the appearance of a peak at its redox potential in the cyclic voltammogram. It can also be used as a quantitative method to measure surface coverage. Ideally, if it is possible for more than one molecule to be present on the surface, their respective redox potentials will fall so they will not obscure one another.

The first attempt to demonstrate OSA on Au and ITO electrodes with electroactive molecules used a carboxylic acid molecule, I, incorporating an alkyl ferrocene redox tag, and a thiol-terminated molecule with a pendant acyl ferrocene group, III. The alkyl ferrocene redox potential is ~300 mV more negative than that of the acyl ferrocene, making them easily distinguishable by cyclic voltammetry.
Deposition of these two molecules simultaneously on Au and ITO surfaces from a solution of 1:1 ethanol/hexane containing a 1000 fold excess of the carboxylic acid (total concentration \( \sim 10^{-4} \) M) is highly selective, Figure 4.1. Cyclic voltammograms of ITO macro- and microelectrodes show a surface confined peak arising from the alkyl ferrocene on the carboxylic acid molecule I, and cyclic voltammetry of the Au electrodes exhibit only a peak from the thiol molecule, III.

This system, although very selective, required the large stoichiometric excess of the carboxylic acid and was judged ultimately less useful than a system with the molecules equimolar in solution. A fair degree of selectivity could be achieved by depositing monolayers from a solution \( 10^{-4} \) M in both I and III in 1:1 ethanol/hexane, Figure 4.2, but surface coverage was low. Reducing the proportion of ethanol to 20 percent by volume and substituting isooctane for hexane substantially improved the surface coverages while maintaining good selectivity, Figure 4.3. A two component solvent system of 5 percent ethanol in isooctane, \( 10^{-4} \) M in I and III, proved to be the most successful of all that were tried, providing rapid monolayer formation, good surface coverage, and selectivity in excess of 100:1 as determined by peak integration and charge ratios, Figure 4.4.

The variations in the characteristics of the deposited monolayers arising from small changes in solvent
Figure 4.1. The electrochemical response of monolayers of an acylferrocene thiol (III) and an alkylferrocene carboxylic acid (I) adsorbed on ITO and Au electrodes from a 1:1 ethanol/hexane solution. The high degree of selectivity in the formation of the monolayers is a result of the large stoichiometric excess of the carboxylic acid.
ITO and Au electrodes derivatized in $10^{-4}$ M RCOOH / $10^{-7}$ M R'SH in 1:1 hexane : ethanol, 24 hours

0.1M (n-Bu$_4$N)PF$_6$/CH$_3$CN

500 mV/sec

ITO, macro

ITO, micro

Au, macro

Au, micro

Potential, V vs Ag wire

Current, $\mu$A

Current, nA
Figure 4.2. Cyclic voltammograms of ITO and Au electrodes derivatized in an equimolar solution of I and III in 1:1 ethanol/hexane. Selectivity and surface coverage is less than ideal.
Orthogonal Monolayer Formation
1:1 ethanol : hexane
$10^{-4} \text{M } \text{Fe(CO)(CH}_2\text{)}_{10}\text{SH/10}^{-4}\text{M Fe(CH}_2\text{)}_{12}\text{COOH}$
Acetonitrile /0.1M (n-Bu)$_4$NPF$_6$ 500mV/sec
Figure 4.3. Cyclic voltammograms of ITO and Au electrodes derivatized in an equimolar solution of I and III in 20 percent ethanol in isoctane. Selectivity and surface coverage of the monolayers is slightly better than from the 1:1 ethanol/hexane deposition solution.
Orthogonal Monolayer Formation
4:1 isoctane : ethanol
$10^{-4} \text{MFcCO(CH}_2\text{)}_{10}\text{SH}/10^{-4} \text{MFc(CH}_2\text{)}_{11}\text{COOH}$
Acetonitrile / 0.1M (n-Bu)$_4$ NPF$_6$ 500mV/sec
Figure 4.4. A successful system for orthogonal self-assembly: ITO and Au electrodes derivatized in a solution equimolar at $10^{-4}$ M in I and III in 5 percent ethanol in iso-octane exhibit highly selective interactions between the ITO and the carboxylic acid molecule and between the Au and the thiol.
Orthogonal Monolayer Formation
95:5 iso-octane:ethanol

$10^{-4} \text{M} \text{Fc CO(CH}_2\text{)}_{10} \text{SH}/10^{-4} \text{M} \text{Fc(CH}_2\text{)}_{11} \text{COOH}$

Acetonitrile /0.1M (n-Bu)$_4$N PF$_6$ 500mV/sec

30 min

15 hours

20 min

15 hours

Current, $\mu$A

Potential, V vs. Ag wire

Potential, V vs. Ag wire
demonstrate the subtlety of monolayer deposition systems. The decrease in the solubility of the carboxylic acid in the two component solvent as the proportion of hydrocarbon increases apparently makes the molecule chemisorb more "aggressively". In general, using a deposition solution which more effectively solvates an adsorbate molecule probably diminishes its tendency to chemisorb at a surface, while reducing its solubility enhances deposition.

It is not possible to determine the extent of monolayer formation on an insulating surface like the Si$_3$N$_4$ substrate in these experiments by cyclic voltammetry. Auger electron spectroscopy (AES), however, which uses a highly focussed electron beam to determine elemental composition on surfaces, works on conductors and insulators. Auger sensitivity varies from element to element, and certain elements, such as C, N, and O, are generally too pervasive in the environment to be useful for analysis. S and F have high Auger sensitivity even in monolayer coverages, and can serve as detection tags for locating monolayers of molecules II and III on surface structures.

To demonstrate the utility of orthogonal self-assembly as a technique for derivatizing surfaces to high lateral resolution, an interdigitated microelectrode array with 4 ITO and 4 Au microelectrodes (~80 µm long x 0.1 µm thick x 2 µm wide, separated by ~2 µm) on an insulating Si$_3$N$_4$ substrate was fabricated, Figure 4.5. An Au/ITO
Figure 4.5. Scanning electron microscope photomicrographs of an ITO/Au interdigitated microelectrode array.
microelectrode array was derivatized from a 5 percent ethanol in isooctane solution of $10^{-4}$ M II and $10^{-4}$ M III, and analyzed by Auger electron spectroscopy, Figures 4.6 and 4.7.

Figure 4.6 shows Auger survey spectra of the Si$_3$N$_4$, ITO, and Au regions of a derivatized Au/ITO microelectrode array. The F peak on the ITO region arises from the adsorbed monolayer of molecule II, and the absence of the F signal on the Si$_3$N$_4$ and Au surfaces confirms the selectivity of the carboxylic acid. The S signal coming from molecule III likewise is present on the Au surface but not the Si$_3$N$_4$ or ITO, showing its high selectivity.

Auger element maps, in which the brightness of a pixel at a given location in the image is proportional to the concentration of the element selected for analysis, are shown for the ITO/Au array, Figure 4.7. The mappings of the elements F, In, Si, and Au are consistent with the conclusion that the carboxylic acid binds only to the ITO and the thiol only deposits on the Au.

**OSA of Phosphonic Acids on ITO and Thiols on Au**

A system of phosphonic acids and thiols present in the same solution at equimolar concentration can orthogonally self-assemble on Au and ITO surfaces in a manner analogous to carboxylic acids and thiols. In general, the phosphonic acids seem to bind to the ITO surface more aggressively than the carboxylic acids, based on their general higher
Figure 4.6. Auger electron spectroscopy (AES) survey scans on the ITO, Au, and Si$_3$N$_4$ surfaces of an ITO/Au interdigitated microelectrode array derivatized in a solution of II and III. The signal for F arising from molecule II appears only on the ITO surface, and the S signal is only on the Au, confirming the selectivities of the carboxylic acid for the ITO, the thiol for the Au, and the exclusion of both from the Si$_3$N$_4$ surface.
Au/ITO Device  CF$_3$(CF$_2$)$_8$COOH : FcCO(CH$_2$)$_{10}$SH

Si$_3$N$_4$ Region

Counts, arbitrary units

ITO Region

Au Region

Kinetic Energy, eV
Figure 4.7. Auger element maps for F, In, Si, and Au from an ITO/Au interdigitated microelectrode array derivatized in a solution of II and III. The F signal is in registration only with the ITO microelectrodes, confirming the selective derivatization of the ITO by molecule II.
tolerance for the presence of H₂O and O₂ during the
depositions, and their persistence during electrochemical
cycling.

Work by Mallouk⁷ using molecule IV suggested that the
phosphonic acids and thiols would be good candidates for a
system for OSA. In that work, this molecule was first
self-assembled on an Au surface via the thiol, then used to
initiate subsequent multilayer attachment through the
phosphonic acid.

Figure 4.8 shows cyclic voltammograms of III and IV
self-assembled onto ITO and Au electrodes from either an
acidified ethanol solution or a 30 percent
ethanol/chloroform solution with \( \sim 10^{-4} \) M concentrations of
each molecule. The presence of the peak from the alkyl
ferrocene in adsorbate molecule IV only on the ITO and the
acyl ferrocene peak of molecule III only on the gold
confirm the high surface selectivity in the formation of
the respective monolayers.

Secondary ion mass spectroscopy was used to
characterize monolayers of III and V self-assembled
orthogonally onto Au and ITO microstructures, Figure 4.9.
Ion maps for \(^{197}\text{Au}^-\) from the Au features, \(^{19}\text{F}^-\) from V,
\(^{115}\text{In}^+\) from the ITO features, and \(^{\text{PO}_2}^-\) (m/z 63) from IV
confirm that the thiol molecule V is only present on the Au
surfaces and the phosphonic acid molecule IV is only on the
ITO.
Figure 4.8. Cyclic voltammograms of monolayers of III and IV self-assembled onto ITO and Au electrodes from either an acidified ethanol solution or a 30 percent ethanol/chloroform solution with \( \sim 10^{-4} \) M concentrations of each molecule. The presence of the peak from the alkyl ferrocene in adsorbate molecule IV only on the ITO and the acyl ferrocene peak of molecule III only on the gold confirm the high selectivity between the materials in the formation of the respective monolayers.
Orthogonal Self-Assembly on ITO and Au

\[ \sim 10^{-3} \text{M } \text{FcCO(CH}_2\text{)}_{16} \text{SH} / 10^{-3} \text{M } \text{Fc(CH}_2\text{)}_{6} \text{PO}_3 \text{H}_2 \]

1:1 Water/Acetonitrile, 0.1M NaClO₄

from Acidified Ethanol (HCl)
12 hours 500 mV/s

from 30 percent Ethanol in Chloroform
30 minutes 200 mV/s

Potential, V vs SCE

Current, µA
Figure 4.9. SIMS ion maps for $^{197}\text{Au}^-$, $^{19}\text{F}^-$, $^{115}\text{In}^+$, and $\text{PO}_2^-$ (m/z 63) on a Au/ITO microstructure exposed to a solution of $\sim 10^{-4}$ M IV and V in 30% ethanol in chloroform for 12 h. The $^{19}\text{F}^-$ signal is in registration with the Au, and the $\text{PO}_2^-$ is in registration with the ITO, confirming the orthogonal self-assembly of the molecules.
Conclusions

Nearly ideal orthogonal self-assembly of monolayers onto microfabricated structures has been achieved using carboxylic acids or phosphonic acids for attachment to ITO and thiols for attachment to Au. Such a system may someday be used to orient molecules between very small pairs of electrodes fabricated from two different materials for the purpose of studying conduction or electron transfer along single molecule chains, or to function as molecule-sized microelectronic devices or sensors.
References


4. Laibinis, P. Harvard University, personal communication of unpublished XPS data taken while a member of the George Whitesides group in September, 1988, indicated that n-alkyl carboxylic acids chemisorbed onto ITO preferentially over n-alkyl thiols present in the same derivatizing solution.


Chapter 5

Diffusion in Solid Frozen Electrolyte Media: Ag⁺ in HClO₄ and Evidence for Two-Phase Behavior
Introduction

The development of microelectrodes with dimensions on the order of a few microns or less has led to the application of electrochemical methods to novel media. These media are frequently characterized by high solution resistance or small volume. For example, microelectrodes have been used to probe gels\textsuperscript{1} and intracellular fluids.\textsuperscript{2} We have used arrays of closely spaced band microelectrodes\textsuperscript{3} (2 \(\mu\)m wide, 2 \(\mu\)m separation) to monitor ion movement in resistive, solid, frozen media. Here we present the results of generation collection and microelectrode transit time (t\textsubscript{m,t}) experiments that were used to characterize the diffusion of Ag\textsuperscript{+} in the frozen glass formed by HClO\textsubscript{4} \cdot 5.5 H\textsubscript{2}O at temperatures between -45 °C and -85 °C, Scheme 5.I. The measurement of time-of-flight\textsuperscript{4} and of diffusion constants via species' transit times\textsuperscript{5} between microelectrodes has been reported for other systems. The temperature dependence of the diffusion coefficient indicates that diffusion is an activated process. Behavior owing to the high-concentration electrolyte solution and phase dependence, however, deviates from diffusion in liquid electrolyte solutions.

Cryoelectrochemistry has been the object of previous scientific study,\textsuperscript{6} and electrochemistry in frozen HClO\textsubscript{4} \cdot 5.5 H\textsubscript{2}O electrolyte in particular has been examined extensively by Stimming et al.\textsuperscript{7} Electrochemical
**Scheme 5.I.** The generation/collection sequence for Ag/Ag\(^+\) starting as Ag plated on one electrode (shown, left) of a microelectrode array. The inter-electrode spacing, d, is 3.0 \( \times 10^{-4} \) cm for this experiment. Ag initially plated on the electrode at left is stripped off by a voltage pulse at an oxidizing potential. The second electrode is held at a reducing potential and re-plates the Ag\(^+\) as it diffuses to the electrode edge, providing a measurable, time dependent collection current.
investigations of frozen solutions are interesting for two primary reasons. First, some interesting physical phenomena occur only at temperatures below the freezing point of liquid solutions. For example, most high $T_c$ materials are conductive below 77 K where most electrochemically useful solvents are frozen.\textsuperscript{8} The electrochemistry of these ceramic materials has been examined at $T > T_c$, and there is significant interest in comparing these properties to the materials in their superconducting state. Second, ion motion is a consideration in solid state electronic devices. The motion of ions in frozen solutions, including glasses and crystals, will serve as model systems for motion in other solid systems.

\textbf{Experimental}

The microelectrode devices used in these experiments were fabricated in the manner previously reported.\textsuperscript{3} Each device consisted of six gold working microband electrodes 80 $\mu$m long, 2 $\mu$m wide, and 1000 Å thick, each separated from its neighboring electrodes by 2 $\mu$m. Also present on each device was a counter electrode 250 $\mu$m long by 300 $\mu$m wide, and 400 $\mu$m away from the working microband electrodes. Alternate working electrodes were pulse-plated with silver for 0.5 s at -0.5 V vs. an Ag wire from a Transene (Rowley, MA) deposition solution, and the counter
electrode was more heavily plated with silver for simultaneous use as a counter and quasi-reference electrode by pulsing to \(-0.5\) V for 2 min.

The temperature controlled electrochemical cell consisted of a glass tube fitted with a ground-glass stopper and two septum-covered inlets at the top end, and an o-ring joint at the bottom used to allow vertical mounting of the microelectrode array, Scheme 5.II. A glass bowl attached at the bottom of the cell held the cold probe from an FTS Systems Flexi-Cool two-stage refrigeration unit, the temperature probe from an FTS Systems TC10 temperature controller, and an isopropanol bath. Temperatures were also checked with an Omega thermocouple probe. The temperature accuracy of the system was about \(+/-\) 2 °C. Perchloric acid was obtained from Mallinkrodt (Paris, KY) or G. Frederick Smith (Columbus, OH), and was diluted to the 5.5 hydrate.

The cell was allowed to equilibrate for at least one hour when initially frozen or after temperature changes. Successive transit time measurements on a given pair of electrodes were made as rapidly as every five minutes.

Instrumentation for this set of experiments included a Pine RDE4E bipotentiostat, a PAR PARC 175 universal programmer, and a Hi Techniques IQ300 digital recording oscilloscope.

Characterization by Auger electron spectroscopy and scanning electron microscopy to verify the movement of Ag
Scheme 5.II. The temperature-controlled electrochemical cell used for measuring transit times of $\text{Ag}^+$ on microelectrode arrays in glassed $\text{HClO}_4 \cdot 5.5 \text{H}_2\text{O}$. 
was done on a Perkin-Elmer Physical Electronics Phi 660 scanning Auger microprobe and a Hitachi S-800 scanning electron microscope.

**Results and Discussion**

The generation and collection of silver ion at adjacent micro-band electrodes in liquid and solid HClO$_4$ · 5.5 H$_2$O demonstrates the motion of the ion, Figure 5.1. Pulsing the silver-plated generating electrode instead of sweeping it anodically produces a peaked distance-dependent current-time plot corresponding to the cathodic current from the re-reduction of silver ions at the collector electrode. A typical unsmoothed trace of the collector current is shown, Figure 5.2. The time measured from the center of a generating pulse to the peak of the collection current is the transit time, $t_{mt}$, and is proportional to the diffusion constant according to the relationship given in equation 1, which is adapted from the Einstein-

$$D = 0.22d^2/t_{mt}$$

Smoluchowski equation. The leading edge of the generator pulse triggers data collection at time zero. The stripping potential was generally in the range +0.8-1.2 V, and the pulse length was always made as short as possible while still giving satisfactory signal-to-noise ratios. Pulses
Figure 5.1. Generation/collection scans for $\text{Ag}^+$ in liquid and solid $\text{HClO}_4 \cdot 5.5 \text{H}_2\text{O}$ electrolyte at pairs of microelectrodes, demonstrating the motion of the ion. The top traces are cyclic voltammograms of the generator electrodes. The bottom waves are collection currents measured as a function of generator potential, with the collector electrode at a fixed reducing potential.
Generation / Collection of Ag\(^+\) in Liquid and Glassed HClO\(_4\)·5.5 H\(_2\)O

Scan rate 50 mV/s on microelectrodes

<table>
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<th>Generator Potential, V vs Ag wire</th>
<th>0</th>
<th>0.2</th>
<th>0.4</th>
<th>-0.2</th>
<th>0</th>
<th>0.2</th>
<th>0.4</th>
</tr>
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<td></td>
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</tr>
<tr>
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<td></td>
<td>20</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Collector Current, nA

Collector held at -150 mV

Collector held at -200 mV
**Figure 5.2.** A current/time plot measured at a collector electrode after a stripping pulse triggered at time 0 at an adjacent generator electrode.
of length up to 1/3 \( t_{mt} \) have been shown to be valid for calculation of diffusion constants. A more complete description of this method for determining diffusion constants has been published previously.\(^5\)

One microelectrode array of six gold band microelectrodes plated alternately with silver would give from approximately ten to one hundred individual transit time measurements. Measurement stopped when depletion of silver and subsequent reduction in current produced unsatisfactory signal to noise ratios.

Repetitive measurement of transit times in the temperature range -45 to -85 °C, when plotted, yielded data distribution histograms as shown in Figure 5.3. Each point on the histogram represents an averaged experiment transit time for the entire set of measurements taken from one microelectrode array at a given temperature. The tendency of the transit times to fall into a faster or slower data grouping suggests that multiple regimes are present in the frozen solid acid electrolyte. Diffusion studies\(^7a,f\) of \( \text{Fe}^{2+}/\text{Fe}^{3+} \) and low-temperature NMR studies\(^7e\) by Stimming et al. also indicate that this system's behavior in the solid state is complex. For the purpose of interpreting our data, two phases were assumed.

Careful cooling, annealing or thawing and refreezing did not make it possible to control which phase would be present at the time of the measurements, suggesting both phases are present simultaneously in a size regime larger
Figure 5.3. Histogram plots of transit times measured from -45 °C to -85 °C. Each plotted point is the average of the set of transit times measured at one microelectrode array.
than the span of the microelectrode array, a distance of 80 μm. In about one out of 30 experiments, two peaks would appear on the current-time plot from the collector electrode, corresponding to an event in which the phase boundary would fall on top of the microelectrode array. Using macroelectrodes for a similar physical measurement of diffusing species would be likely to average the values for the two phases.

Histograms were made for the data set of transit times at each temperature, Figure 5.3. These histograms were then partitioned into a faster and slower regime, and the set of averages in each regime averaged. This yielded an average fast and slow transit time at each temperature, from which the Arrhenious plot for the activated process of diffusion could be made, Figure 5.4. The activation energies for the diffusion of silver ion in each phase of frozen perchloric acid are 6.8 kJ/mol for the slower phase and 7.0 kJ/mol for the faster phase. The pre-exponential factors are, however, substantially different. It is significant that the activation energies are essentially the same in each phase, indicating that the mechanism of diffusion is probably the same in both cases.

**Conclusions**

Transit time measurements are an effective method for studying the diffusion of Ag⁺ in solid, frozen HClO₄ · 5.5
Figure 5.4. Arrhenious plots of the diffusion constants of Ag⁺ in solid and liquid HClO₄ · 5.5 H₂O. The activation energies for diffusion of Ag⁺ ion in frozen HClO₄ · 5.5 H₂O are 6.8 kJ/mol in the slower phase and 7.0 kJ/mol in the faster phase.
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**Table 5.1.** Transit times ($t_{mt}$) and diffusion constants ($D$) for $\text{Ag}^{+}$ ion in both phases of solid $\text{HClO}_4 \cdot 5.5\text{H}_2\text{O}$ over the temperature range -45 to -85 °C, and in liquid from -20 to -35 °C.
H₂O. This electrolyte exhibits complex behavior in the solid state, with phase domains larger than ~80 µm. By assuming the presence of two phases and partitioning the data at logical points, activation energies for diffusion of Ag⁺ ion in frozen HClO₄ • 5.5 H₂O calculated from Arrhenius plots are 6.8 kJ/mol in the slower phase and 7.0 kJ/mol in the faster phase. Frozen HClO₄ • 5.5 H₂O has also proven to be an effective highly acidic, solid electrolyte which could lend itself to extending studies of measuring switching speeds of polyaniline in this medium⁹ by taking advantage of the transistor configuration of polyaniline on a microelectrode array.¹⁰
References


