#### **RESEARCH PROPOSAL**

## Applications of Organomercaptan Self-Assembled Monolayer-Based Microelectrode Arrays for the Study of Nanometer-Scale Electrode Processes

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#### I. INTRODUCTION

In the field of electrochemistry, there is an ongoing interest in the development and characterization of very small electrodes. The advantages of performing electrochemical studies at micron and submicron-scale electrodes are well-documented.<sup>1-3</sup> First, the signal to noise ratio is enhanced due to lowered capacitative current and increased rates of mass transfer to the electrode surface. Second, decreased iR<sub>s</sub> loss results in more reliable potential measurements. This advantage also allows for experimentation at higher scan rates and in non-conducting solvent systems. Finally, small size has permitted for electrochemical study of in vivo processes<sup>4</sup>. These advantages have lead to the application of microelectrodes and microelectrodes arrays in a variety of analytical detection schemes, including applications in liquid chromatography<sup>5</sup>, capillary electrophoresis<sup>6</sup>, studies of single cell exocytotic processes<sup>7,8</sup> and as a mean of sensing trace environmental contaminants<sup>9,10</sup>.

To realize the full benefits of sub-micron scale electrodes it is necessary to understand the electrochemical processes which occur as the size of the electrode approaches molecular dimensions. In the literature, deviations from classical microelectrode behavior are predicted when very small electrodes are employed.<sup>11-13</sup> Physical phenomena not accounted for in the mathematics of traditional microelectrode theory are implicated in this behavior. These phenomena include merging of the electrical double-layer and diffusion regimes, as well as enhanced fluid density and viscosity effects in the double-layer region. Fabrication difficulties and a lack of precise knowledge of electrode geometry have been an obstacle in attempts to probe for these deviations. Lewis and Oldham have shown that it is necessary to have knowledge of the true electrode geometry in order for accurate information about electron transfer kinetics to be obtained.<sup>14,15</sup> A primary objective of the research proposed here is to address the issue of electrochemical behavior at nanoscale electrodes. Electrode arrays fabricated by performing a cyanide-etching procedure on a hexadecanethiol self-assembled monolayer may be produced having individual electrode diameters ranging from 10-50 nm. The geometry of these electrodes may be determined by STM (scanning tunneling microscopy), and the results employed to calculate theoretical limiting current behaviors based on a variety of model systems. Comparison of these results with the experimental electrochemistry provides a means of probing for deviation from traditional microelectrode theory. Also, a variety of redox probes will be selected to examine for possible molecular recognition effects as the size of the electrode approaches that of the electroactive species.

Other studies being proposed include the application of the electrode arrays as template sites for constructing hemispherical electrodes from thiolated gold colloids and employing the arrays to examine possible methods to prevent localized corrosion processes. Finally, experiments will be proposed to determine the feasibility of employing the arrays as possible sites for enzyme-immobilization and biocatalysis.

#### **II. BACKGROUND**

# **Characterization of Microelectrodes and Microelectrode Arrays**

The opportunities provided for the study of fast electron transport processes,<sup>16</sup> detection of trace analytes and electrochemistry in nontraditional media has prompted a sustained creative effort directed at the fabrication and characterization of microelectrode devices. Some of the strategies which have been used to produce single microelectrodes include sealing platinum wire or carbon fiber in glass,<sup>17</sup> deposition of mercury on a platinum or

iridium substrate,<sup>18,19</sup> patterning of an alkanethiol monolayer resist by STM lithography<sup>20</sup> and sealing a metal foil or deposited metal layer between two insulating layers to produce a band electrode.<sup>21</sup> Much effort has also been devoted to the production of microelectrode arrays. Arrays offer increased current detection efficiency due to the summation of the currents from the individual elements in the array. Microelectrode arrays have been produced by electrochemically etching carbon fiber-epoxy composites,<sup>23</sup> sonochemically ablating polymer films,<sup>24</sup> sealing layers of carbon fibers in an epoxy-glass matrix,<sup>25</sup> applying electron bean lithography to a poly (methyl methacrylate) resist<sup>26</sup> and depositing Au into aluminum oxide micropores,<sup>27</sup> among other techniques.

Work published by Alan Bard, Henry White and Charles Martin is of particular interest to the research being proposed here. Bard's group has done extensive characterization of microelectrodes designed to be used as tips in scanning electrochemical microscopy (SECM).<sup>28,29</sup> This technique is designed to probe surface topography and electrochemical behavior by measuring the faradaic current at an ultramicroelectrode probe as it approaches a sample substrate. This technique has proven successful in single molecule detection, where a stochastic current response indicative of oxidation of a single molecule trapped between a wax-coated Pt/Ir tip and a conducting substrate has been observed.[Fan, 1996 #8; Fan, 1995 #3946] Interestingly, in single molecule experiments, the microelectrode current was shown to be dependent on electrolyte concentration, a fact which might be related to the effects of migration on the electrochemical response.

Menon and Martin have fabricated nanometer-sized microelectrode arrays by performing an electroless deposition step on a nuclear "track-etched" polycarbonate membrane<sup>31</sup>. This method has been employed to produce gold nanowire electrode ensembles with diameters as small as 10 and 30 nanometers. The 30 nm electrodes exhibit an electrochemical response in agreement the predicted response for a macroelectrode of identical active area. In the case of the 10 nm electrodes however, a decrease in the peak to peak cyclic voltammetric current was observed accompanied by diminished redox reversibility when increased concentrations of supporting electrolyte were employed.

White and coworkers studied the electrochemistry of a series of nanometer-scale band electrodes in the presence of the redox probes ferrocene and decamethylferrocene. The band electrodes used in this study were fabricated by depositing platinum or gold films on cleaved mica substrates. The electrodes in these experiments exhibited increased selectivity for the smaller redox probe as the size of the electrode approached that of the analyte. It was also discovered that the experimental and theoretical limiting currents were in agreement for electrodes  $\geq 20$  nanometers in width, however, for smaller electrodes the limiting currents were an order of magnitude less than predicted.<sup>32</sup>

#### **Characterization of Organomercaptan Self-Assembled Monolayers (SAMs)**

The characterization of alkanethiol monolayers bound to gold has been a subject of much research. Thiol monolayers have been studied by optical ellipsometry, contact angle analysis, a variety of surface sensitive infrared techniques and STM, among other methods. These studies have shown that long chain alkanethiol monolayers form well-packed crystalline-like structures, with the alkane chains tilted 20-30° from the surface normal. Shorter chain thiols form more sparsely packed disorganized structures.<sup>33</sup> On Au(111) substrates, such as the Au ball facets being used in these studies, it has been shown that the monolayers form close-packed ( $\sqrt{3} \times \sqrt{3}$ ) - R30° overlayers on the gold, and that the underlying gold structure is reflected in the triangular etch patterns induced by cyanide etching performed under potential control.<sup>34</sup>

The electrochemical blocking ability of the SAMs is correlated with monolayer hydrophobicity and the absence of bulky end groups which decrease monolayer packing efficiency.<sup>35</sup> Passivating ability increases with alkanethiol chain length and is maximized by lengthening the soaking time of the substrate in an ethanolic thiol solution.<sup>33</sup> Where alkanethiol passivating ability is not satisfactory, it is possible to improve blocking ability by employing an electrochemically polymerizable species to fill in pinhole sites.<sup>36</sup>

The porosity of alkanethiol SAMs has been employed as a model microelectrode system for the study of fast electron transfer processes, where Amatore's work on the scan rate dependence of the linear to radial

diffusion transition may be used to gather indirect knowledge of the monolayer pinhole density.<sup>37</sup> Studies of this type necessarily assume that electrochemical behavior at nanometer-scale pinhole sites is identical to behavior at larger electrodes systems. Intentionally created defects in the monolayer have also been studied as a means of gaining knowledge about electrode surface processes. Studies of mixed monolayers of long-chain alkanethiols and short aromatic thiols have demonstrated monolayer molecular recognition properties, as well as a dependence of the electrochemical response on electrolyte concentration.<sup>38,39</sup>

## **III. TECHNIQUES**

#### **STM and ECSTM Characterization**

STM (scanning tunneling microscopy) is used to characterize conducting surfaces with angstrom, or atomic-scale resolution, as well as to examine micron-scale surface topology. A tunneling current is passed between a very sharp tip and a substrate, while a potential ( $V_{bias}$ ) is maintained between them. The tunneling current is dependent on the overlap of the tip and substrate wavefunctions and may be described by the following equation.

$$I = C \rho_t \rho_s e^{s \sqrt{\phi}}$$
(1)

where I describes the tunneling current, C is a function of the voltage maintained between the tip and the surface,  $\rho_t$  and  $\rho_s$  are functions of the electron densities of the tip and substrate respectively, and  $\phi$  is a work function relating to the tip-sample barrier.<sup>44</sup> STM experiments may be performed in constant height or constant current mode. In constant current mode a feedback loop operating on a piezoelectric is employed to maintain a set current between tip and the sample. This mode allows for a topographical mapping of the sample. In constant height mode, the feedback effect is minimized so that the electronic interactions between the sample and the tip



Figure 1: Diffusion behavior of microelectrode arrays

may be directly monitored. This mode allows for mapping of the electronic features of the sample, and is particularly useful in atomic-scale studies.

In EC-STM (electrochemical scanning tunneling microscopy) the potential between the tip and the sample ( $V_{bias}$ ) as well as the potential of the tip and sample in relation to a reference electrode ( $V_{tip}$  and  $V_{sample}$ ) are operator controllable. This allows surface morphology to be examined under different electrochemical potentials, and is particularly useful for deposition and corrosion studies.

#### Electrochemistry

Cyclic Voltammetry (CV) is an important technique for the studies being proposed here. This technique is noted for its sensitivity and can provide information about electrode reaction mechanisms and redox reversibility. This technique allows the current at a working electrode to be monitored as its potential is scanned through a triangular-1 potential wave. The important parameters in a cyclic voltammgram are

agnitude of the peak current and the separation between the anodic and

cathodic peak potentials. Cyclic voltammograms are peak-shaped for macroelectrodes as a result of linear diffusion to the electrode surface. Single microelectrodes exhibit a sigmoidal-shaped CV resulting from radial diffusion. For microelectrode arrays, the shape of the current response is dependent on geometry of the array and the scan rate. The polarogram, or sigmoidal, limiting current response is recorded when the proper scan rates and electrode separations are employed. (See Figure 1)

Other techniques should prove helpful in these studies including AFM (atomic force microscopy), EC-AFM (electrochemical atomic force microscopy) and impedance analysis. AFM relies on a mechanical interaction between a cantilever bound tip and the sample in order to produce an image of the surface. EC-AFM provides for

independent control of tip and substrate potentials, permitting electrochemically induced surface changes to be imaged in solution. Impedance analysis provides information about conductivity at the solution-electrode interface by invoking a model of the electrochemical cell based upon en electrical circuit. I am also interested in applying the *in situ* QCM (quartz cyrstal microbalance) and FTIR-ERS (fourier transform infrared external reflectance spectroscopy) as a means of monitoring the growth of nanostructures composed of gold colloids or polymeric species at the microelectrode template sites. QCM employs a piezoelectric to translate the mechanical signal induced by mass changes on the surface to an electronic signal. FTIR-ERS detects the vibrational absorbtion energies of species on the surface.

# **IV. PRELIMINARY RESULTS**

My initial studies have focused on preparing microelectrode arrays by etching self-assembled monolayers in alkaline cyanide solution under potential control. Etching at native Au defect sites results in corrosion induced pitting of the surface, and subsequent removal of the passivating thiol layer. This process has been studied by several different research groups. [Kirk, 1980 #75; Kirk, 1978 #71; Cathro, 1964 #72; MacArthur, 1972 #73] The mechanism proposed by Foulkes and Kirk, applicable to etching at low overpotentials, is described by the following three-step dissolution process.

 $\begin{array}{rrrr} Au + CN^{-} \leftrightarrow AuCN_{ads}^{-} \\ AuCN_{ads}^{-} \rightarrow AuCN_{ads} + e^{-} \\ AuCN_{ads} + CN^{-} \leftrightarrow Au(CN)_{2}^{-} \end{array}$ 

*In situ* ECSTM experiments have shown that the presence of an alkanethiol monolayer will inhibit this dissolution process, and push the onset of corrosion to higher overpotentials.[Zamborini, 1997 #5] The presence of a Cu UPD layer on the Au(111) surface further inhibits this corrosion process and also increases the potential window of electrochemical stability.[Zamborini, #6]



The fabrication procedure is illustrated in Figure 2. The substrate is an Au ball prepared by annealing a 99.99% purity Au wire in an  $H_2/O_2$  flame. The annealing process produces facets containing atomically smooth Au(111) terraces. The facets make it possible to produce well-resolved images of the surface on the micron and sub-micron scale. The facet is isolated with apiezon wax to restrict the electrochemistry to the Au(111) surface. The surface is then cleaned by cycling electrochemically in acidic media, and a Cu-UPD layer is added to the surface before soaking in ethanolic hexadecanethiol solution overnight.

The next step is to examine the surface for electrochemical passivation prior to the etching process. The

probe used for these experiments is 5mM Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>/.1M K<sub>2</sub>SO<sub>4</sub>. es which exhibited passivation (tunneling current rather that faradaic t is observed in the cyclic voltammetry) were then exposed to alkaline cyanide solution under potential control. At this time, the etching

process may be monitored amperometrically to allow greater control over the fabrication procedure. The sample is then rinsed thoroughly and cycled again in the redox probe solution. Samples having a polarogram-shaped CV indicative of radial diffusion are retained for STM analysis while samples exhibiting linear diffusion are discarded. For the results described here, ten STM images were employed in the image analysis process. The analysis produced the following variables which were employed in the model calculations, R<sub>ave</sub> (the average electrode radius) and N (the number density of electrodes on the surface).

The microelectrode models employed include the inlaid disc, the recessed disc and the ring electrode models. (See Figure 3) The recessed disc model is similar to the inlaid disc model but assumes that the electrode

Figure 3: Microelectrode model systems

is surrounded by an insulating monolayer of height L.[Bond, 1988 #76] In these experiments the inslating layer is the hexadecanethiol monolayer whose height is 2.1 nm. Equations (2) and (3) describe the limiting current density arising from the inlaid and recessed disc electrodes, where F is faraday's constant (96,500 Coulombs/eq), n is the number of electrons transferred, D is the diffusion coefficient for the redox probe and C is the concentration of the redox species.

$$i_{lim} = 4nFR_{ave}CDN$$
 (2)

$$\dot{i}_{\rm lim} = \frac{4\pi n F R_{\rm ave}^2 CDN}{4L + \pi R}$$
(3)

The ring electrode model is described in equations (4) and (5). This model was developed by Szabo and may be applied when the outer radius of the ring ( $R_0$ ) is much larger than the inner radius of the ring ( $R_1$ ). Preliminary metal deposition experiments have shown that metals tend to accumulate in a ring-shaped pattern around the edge of the etch pits, a result which prompted the application of the ring electrode model for this system. For the calculations, we assume an arbitrary electrode ring width of .5 nm

(5

$$i_{lim} = wnFCD$$
 (4)

where

Figure 4: Result of a single etching experiment
a) 1 μm<sup>2</sup> STM image with electrode circled in white b) CV in 5 mM Ru(NH<sub>3</sub>)<sup>3+</sup>/.1 M K<sub>2</sub>SO<sub>4</sub>
c) CV in 5 mM Ru(NH<sub>3</sub>)<sup>3+</sup>/.1 M K<sub>2</sub>SO<sub>4</sub> after etching

$$w = \frac{\pi^{2}(R_{i} + R_{o})}{\ln \left[ 4e^{3/2} \binom{R_{i} + R_{o}}{R_{o} - R_{i}} \right]}$$

Figure 4 shows STM and electrochemical data from a successful etching experiment. The STM image

is of a triangular-shaped microelectrode formed after cyanide etching of the substrate. Before etching, the cyclic voltammetry response shows that the sample is electrochemically passivated. After etching a final limiting current of 340 nA is obtained. The shape of the final voltammetry indicates that radial diffusion is the primary mode of mass transport to the electrode. The results from the model calculations for this sample are shown in Table 1. Here we can see that the experimental limiting current behavior is most closely approximated by the recessed disc electrode model. This result is common to four of the five analyzed samples. For all of the samples examined the predicted limiting current response is greater than the experimentally observed response. Further interrogation of the data shows a correlation between the electrode number densities and the deviation values. Standard microelectrode theory predicts a radial diffusion dominated microelectrode-type response for electrode arrays whose individual electrode diameters are smaller than  $10 \cdot R_{ave}$ . This result is particularly interesting since the STM data indicates the majority of the alkanethiol-based microelectrodes prepared fulfill this criterion.

Sample <sup>a</sup>	Average	Electrode	I <sub>lim</sub>	I <sub>lim</sub> STM	I <sub>lim</sub> STM	I <sub>lim</sub> STM	I <sub>lim</sub> STM
•	Electrode	Number	Experimental	Ring	Inlaid	Recessed	Recessed
	Radii	Density	$(nA)^{c}$	Electrode	Disc (nA)	Disc (nA)	Disc/I <sub>lim</sub>
	(nm) <sup>b</sup>	(electrode/µm <sup>2</sup> ) <sup>b</sup>		(nA)			Experimental
1	23±9	2±3	340	2300	2600	1700	7
$2^d$	13±11	1±1	85	240	300	200	3
3	13±4	6±4	300	2900	4200	3400	11
4	5±2	8±6	130	1500	2000	1300	10
5	13±4	1±2	120	600	800	700	6

 Table 1: Microelectrode Array Experimental and Theoretical Limiting Currents with STM Determined Parameters

<sup>a</sup> Samples were etched C<sub>16</sub>SH monolayers on Cu-UPD modified Au(111). <sup>b</sup>Average Radii and Electrode Number Density data were obtained by analysis of ten .25  $\mu$ m<sup>2</sup> STM images, unless otherwise indicated. The pit area was determined at a threshold depth 3 Au atomic step heights below the mode feature height of the image. <sup>c</sup>Cyclic Voltammetry was performed in 5mM Ru(NH<sub>3</sub>)<sub>6</sub><sup>3+</sup>/ .1M K<sub>2</sub>SO<sub>4</sub>. <sup>d</sup> STM parameters were obtained by analysis of ten 1  $\mu$ m<sup>2</sup> STM images.

#### V. PROPOSED RESEARCH

The preliminary results show that nanoscale electrodes of well-characterized geometries may be fabricated from alkanethiol monolayers. The results also indicate their utility for probing electrochemical phenomena at very small electrode surfaces. The objective of my proposed research is fourfold. First, the analysis and characterization of the electrode arrays will be refined in an attempt to establish a relationship between the electrode number densities and limiting current deviations. This will entail a series of experiments designed to establish the electroactivity of the etch pits and the realization of a more precise model system for the electrode arrays. Second, the arrays will be investigated for possible molecular recognition effects using a variety of electroactive redox probes, including a series of electroactive dendrimer molecules. Third, the arrays will be employed as template sites for growing isolated nanostructures. Structures prepared form selectively



I. My previous work has shown that the experimental and theoretical limiting current behaviors for these nanometer-scale microelectrodes differ, on average, by slightly less that an order of magnitude. The difference between these values appears to be correlated to the electrode number densities as determined by STM. Establishing a method for controlling the number densities of the individual electrodes in the array will be necessary if this point is to be proven definitively.

One way to control the electrode number density is to engineer defect sites into the monolayer where preferential etching will occur. I will etch monolayers prepared from mixed solutions of short aromatic and long-chain alkanethiols in order to establish control of the electrode distributions.(See Figure

5) The electrode number densities obtained should be directly related to the ratio of short aromatic to long chain thiol employed in the soaking solution.

Another method I would like to explore as a means of controlling the electrode distribution is the UVinduced photoxidation of a hexadecanethiol monolayer. The photoxidaton process occurs at a precise UV wavelength.and may be controlled by limiting the exposure time of the monolayer to the UV source. Initially, the oxidation process occurs randomly throughout the monolayer, which should provide a more even distribution of electrode sites in the monolayer.

I am also interested in developing a model for the electrode arrays which will take into account geometrical irregularities of the individual electrodes. Preliminary calculations have assumed a circular geometry for the individual electrodes. STM has shown, however, that the electrodes are often triangular or rectangular in shape. Determining a method for including these irregularities into the model calculations will help validate my findings regarding nanoscale electrochemical processes.



II. Establishing the degree of electroactivity of the etch pits is a crucial aspect of this research proposal. I will investigate this issue by performing several different experiments. First, I will measure the double layer charging current before and after etching. Since the double layer charging current from the monolayer is negligible, charging current measured after etching is produced by the electroactive area of the etch pits.

Another method to determine the electroactive area of the arrays is by ac impedance. The area measurement may be performed by measuring the charge transfer resistance of the array after etching in the presence of a redox probe of known heterogeneous electron transfer rate. The area may also be determined by scanning positively through the gold oxidation wave, or by assembly of a ferrocene-terminated thiol into the etch pits. The magnitude of the ferrocene redox wave may be employed to determine the electroactive pit area. Finally, copper may be deposited into the etch pits while monitoring the deposition by EC-STM. The latter technique is least favorable due to for copper accumulation in electroinactive areas due to the possibility for dendritic growth.

An additional study will be performed to obtain the  $RC_d$  current decay time constant of the arrays following a potential step. This study will provide information about the capacitance of the array, which is the intrinsic limiting factor in efforts to obtain kinetic parameters in fast electron transfer processes. If the capacitance is adequately low, it may be possible to apply the arrays for a variety of kinetic studies.

Finally, the effects of different concentrations of electrolyte on the voltammetry will be examined, and a thorough investigation of the stability of the electrode arrays will be undertaken.

III. Molecular recognition effects will be examined for a variety of redox probes, including ruthenium hexaamine, a number of water-soluble ferrocene derivatives, benzyl viologen and a variety of benzyl viologen terminated dendrimers currently being studied and synthesized within the Crooks group. PAMAM dendrimers are branched

macromolecules composed of repeating subunits of ethylenediamine and polyamidoamine originating from an ethylenediamine core. The benzyl viologen dendrimer derivatives are of particular interest since they are water soluble (which is convenient for the electrochemical studies) and have a redox potential within the range of stability of the thiol monolayer.(See

Figure 6) These dendrimer molecules provide an excellent vehicle for examining molecular recognitioneffects on the electrochemistry of very small electrodes since they provide an assortment of available sizes, ranging up to several nanometers in diameter. The extent of dendrimer functionalization may be determined by NMR, and the diffusion coefficients necessary for the model calculations may be obtained by chronoamperometry at a single microelectode of standard dimensions. IV.

### **V. CONCLUSIONS**

A method for fabricating nanometer-scale microelectrode arrays has been proposed which will provide an opportunity for the study of the effects of electrode size on electrochemical processes.

Figure 7: Assembly of gold colloid nanostructure at microelectrode etch sites	
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# Figure 6: Fourth generation benzyl viologen terminated dendrimer

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